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UNIVERSITY PHYSICS

BY

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PART TWO

HEAT
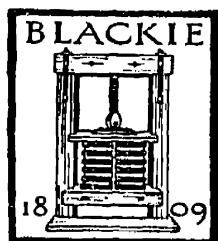
PREFACE

This book is primarily intended for students taking a First and Second Year Course in Physics at a University. It is designed for preparation for examinations of the standard of Part I of the Natural Sciences Tripos at Cambridge, the B.Sc. General Degree of London and, by the omission of those sections marked with an asterisk, for Intermediate students who have already studied the elements of Physics at school or elsewhere.

It must be remembered that at the stage covered by this book, students will not yet have become specialists in Physics. The writer has had frequent experience of students who, during a period when they are studying two or three additional subjects, feel a great need for **one book** on Physics which contains the basic information which they must acquire. It is not suggested that this book has made others unnecessary or, more particularly, that it has rendered lectures superfluous. It remains as important as ever for students to read widely and to acquire experience of the different methods of treatment of a subject which only a diversity of Lecturers can supply.

Finally, it is becoming more and more recognized, at least as an ideal, that material usually given in formal lectures can be quite as well acquired from good text-books and that lectures will gradually develop into a tuitional tutorial system under which the time and energy of the lecturer can be devoted to the detailed elucidation of difficult points, apt illustrations and demonstrations, the discussion of essays and exercises done by the student, and the exercise of personality to engender an enthusiasm without which a subject remains " dry bones ".

F. C. CHAMPION.

CONTENTS

PART II

HEAT

CHAPTER I

Temperature and Thermometry

1. Introduction.

We commence our study of Heat with considerations of Temperature. Over a limited range, **temperature** is a concept which is directly appreciated as a sense perception and we may define it as the **degree of hotness of a body**. A more precise definition requires a considerable knowledge of heat phenomena and we shall not attempt it at this stage. We may note, however, that temperature receives a ready explanation on the molecular hypothesis (Chap. XI), where it is identified with the kinetic energy of the molecules.

2. Scale of Temperature.

Most people have little difficulty in distinguishing the temperatures of different bodies over a limited range if the temperature difference is large, but it requires great skill, experience and aptitude to detect a temperature difference of $\frac{1}{4}°$ C. Again, wood and metal, although actually at the same temperature, appear to be at different temperatures if they are judged by touch. We therefore need a means of estimating temperature which is (*a*) more reliable and objective, (*b*) more sensitive, than direct determination from the sense of touch. Any physical property which changes continuously with temperature, e.g. length, volume, gas pressure, electrical resistance, &c., may be used to measure temperature. Most of these physical properties increase in magnitude with increased temperature, but they do not all increase at the same rate or in the same way. For example, while we might define the temperature θ_2 at which a wire had twice the electrical resistance it possessed at a temperature θ_1 by the relation $\theta_2 = 2\theta_1$, we should not in general find that the volume or length of bodies was doubled on raising the temperature from θ_1 to θ_2. **Each physical property therefore has its own temperature scale.** Because of the interdependence of physical phenomena the different temperature scales are connected, and, as we shall see (section 6, Chap. XIII), it is even possible to define an **absolute scale of temperature.**

3. The Centigrade Scale.

The melting-point of ice and the boiling-point of water take place at definite temperatures if certain conditions are fulfilled. If these two

temperatures are called 0° and 100° respectively, they are said to represent two *fixed points on the Centigrade scale*. Now the melting-point and boiling-point depend very much on the purity of the substance. They also vary with changes of external atmospheric pressure. As pure water is easily obtained it is suitable for giving the fixed points and accordingly **0° C. is defined as the temperature of melting ice under an external pressure of 760 mm. of mercury at sea-level and latitude 45°, while 100° C. is the boiling-point of water under the same conditions.**

When two fixed points have been determined, other temperatures are related to these by the *Centigrade definition*, namely

$$t° = (A_t - A_0)/\{(A_{100} - A_0)/100\}. \qquad . \quad . \quad . \quad (1)$$

In equation (1), A_t is the magnitude at temperature $t°$ of the physical property which is being used to measure the temperature $t°$, A_0 is the magnitude of that quantity at 0° C. and A_{1c0} its value at 100° C. Equation (1) may therefore be expressed as

$$t° = \frac{\text{Change in magnitude of property}}{\frac{1}{100} \text{ (change in magnitude of property on raising from } 0° \text{ to } 100°)}.$$

To fix ideas, let us suppose A represents the length of the mercury column in a mercury thermometer. Then from (1)

$$t_l = (l - l_0)/\{(l_{100} - l_0)/100\}, \qquad . \quad . \quad (2)$$

Fig. 1.—Mercury Thermometer

where l_{100} is its length at 100° C., l_0 its length at 0° C., and l its length at t_l. Equation (2) therefore defines t_l and allows it to be calculated.

4. Common Mercury Thermometer.

The name **thermometer** is given to any instrument which is used to measure temperature. The name **thermoscope** is usually reserved for instruments which register a single temperature. For example, the action of an electric fuse depends on one temperature only, that of its melting-point, and thus it constitutes a typical discontinuous thermoscope. The commonest type of thermometer is the liquid-in-glass thermometer, the liquid usually being mercury.
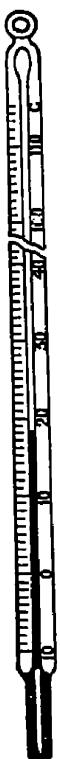
The mercury thermometer, as shown in fig. 1, consists of a bulb blown at the end of a glass tube of capillary bore. Clean dry mercury is introduced by alternate heating and cooling until all the air is expelled and the whole is filled with mercury. While the mercury is still hot and occupying the whole of the bulb and tube, the top end of the

tube is sealed. On allowing the thermometer to cool, the mercury contracts until at room temperature it is standing a few centimetres above the bulb. The instrument is now calibrated by immersing the bulb first in melting ice as shown in fig. 2, and then **in the steam** from boiling water as shown in fig. 3. Scratches are made on the glass tube opposite the level of the mercury under the two conditions and the figures 0° and 100° are engraved on the tube. The space between the 0° and 100° is then subdivided into 100 equal parts, figures being engraved on the
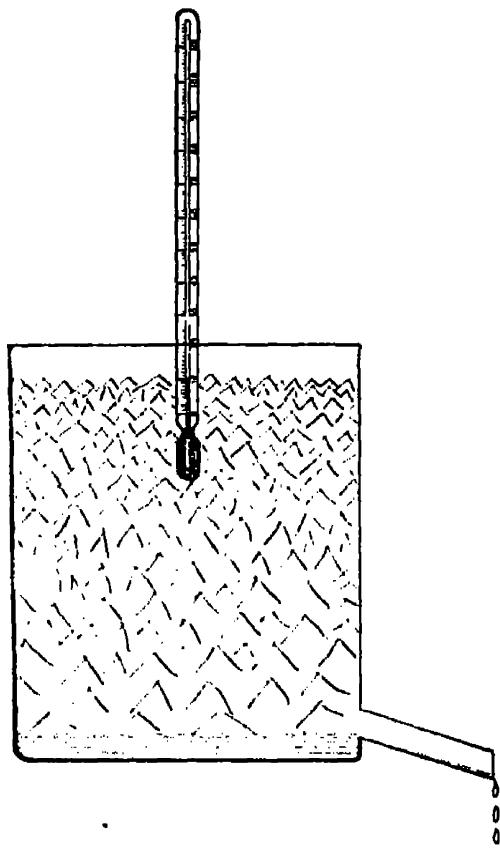

Fig. 2.—The Zero-point
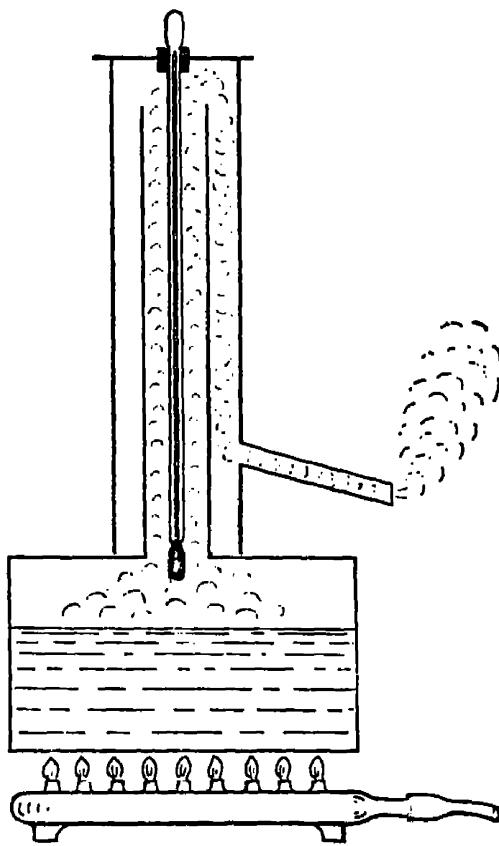
Fig. 3.—The Boiling-point of Water

tube at suitable intervals. Such division is termed **interpolation;** the scale may also be **extrapolated** below 0° C. and above 100° C. by continuing the uniform divisions beyond these temperatures.

5. Some Temperature Scales.

One of the earliest thermometers on record was that devised by Galileo. It consisted of an inverted glass bulb containing air. The neck of the bulb dipped into a reservoir of coloured liquid. Rise of temperature resulted in expansion of the air and change in position of the level of coloured liquid in the neck. Galileo also made a liquid-in-glass thermometer, using alcohol as the working substance. For many years, however, temperature scales remained quite arbitrary, partly owing to the difficulty of obtaining pure working substances and partly because it was not realized that fixed points could be obtained simply from melting- and boiling-points of suitable materials.

Little progress was made until 1701, when Newton proposed a

scale of temperature, defining 0° on the scale from the melting-point of ice and 12° as the temperature of the blood of a healthy man. On this scale, the boiling-point of water, which was regarded as too variable to be suitable for a fixed point, came to 34°. The working substance used was linseed oil. In 1714, a great step forward was made when **Fahrenheit** introduced mercury as the working substance, for this is comparatively easily purified. Fahrenheit introduced at the same time a scale of temperature which is still widely used in meteorology and medicine. This persistence is unfortunate, since the fixed points on Fahrenheit's scale were most unsuitable for scientific work. The lowest temperature reached by an unrecorded mixture of ice and sal-ammoniac was taken as 0° F. and the warmth of the human body as 96° F. On the same scale, the melting-point of ice is 32° F. and the boiling-point of water is 212° F.

A third scale which is sometimes used is due to Réaumur. On this scale the fixed points are 0° R. at the melting-point of ice and 80° R. at the boiling-point of water.

To convert temperatures from one scale to another the ratios of two given intervals are equated; hence

$$\frac{C}{100} = \frac{F-32}{180} = \frac{R}{80}. \quad \cdot \quad \cdot \quad \cdot \quad (3)$$
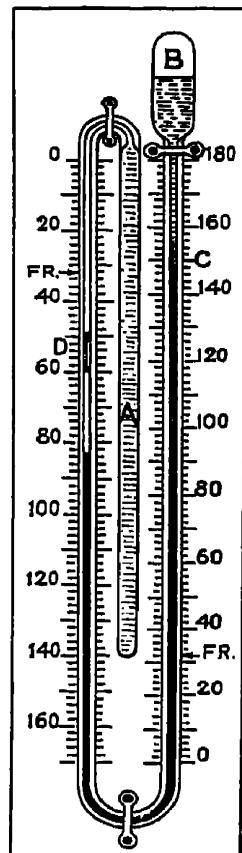
6. Types of Thermometer.

(a) Liquid-in-glass Thermometers.

(i) *Six's Maximum and Minimum Thermometer.*

Fig. 4. — Six's Maximum and Minimum Thermometer.

In this thermometer, a cylindrical bulb A as shown in fig. 4 is filled with alcohol which extends continuously up to the mercury column. More alcohol is situated beyond the mercury column, and finally an air and vapour space B exists at the far end of the tube, which is closed. Two small steel indices C and D are in contact with the ends of the mercury column. If the temperature rises, the volume of the alcohol in A increases and the mercury column is pushed round, driving the index C before it. If the temperature should now drop, the index C remains in its farthest position and thus indicates the **maximum** temperature which occurred. Conversely, the position of D indicates the **minimum** temperature reached. The indices are returned to the ends of the mercury column by the use of a magnet.

(ii) *Clinical Thermometer.*

This is an ordinary mercury thermometer except that it possesses a very fine constriction in the capillary bore, visible in fig. 5.

On inserting the bulb into the patient's mouth (say) the mercury expands and indicates its appropriate temperature. On removal from the patient, the mercury stays at its highest position, for the thread
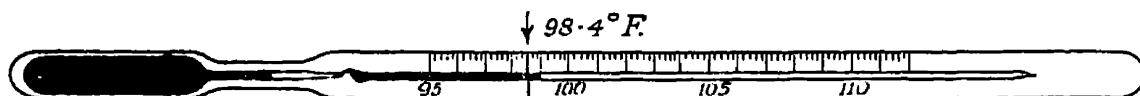

Fig. 5.—Clinical Thermometer

simply breaks at the constriction as the main bulk of mercury in the bulb contracts. The entire scale is made to cover only some 10° F., so fractions of a degree are easily observed. The short column of mercury is returned to the bulb by shaking.

(iii) *Beckmann Thermometer.*

This thermometer is designed to read **differences** of temperature to $\frac{1}{100}$° C. As shown in fig. 6 it consists of a large bulb A containing mercury and connected with the usual capillary stem B, graduated with five or six large divisions each corresponding to 1° C. and each subdivided into 100 equal parts. So that the instrument may be used over a large range of temperature, the bulb C is constricted at the top end of the thermometer. Mercury is then jerked over from A to C or vice versa so that when the bulb A is immersed in the vessel whose temperature **change** is required, the mercury stands at a convenient height in the stem B.

We shall discuss other types of thermometer only very briefly in this chapter. Their use depends upon a knowledge of a variety of physical phenomena which are discussed in detail in the chapters concerned.

(*b*) **Gas Thermometers.**

These may be of the constant pressure or constant volume type. In practice, the **constant volume thermometer** described in detail in Chap. VII constitutes the basic thermometer against which all others are calibrated. The scale of temperature defined by the constant volume hydrogen thermometer is referred to as the **gas scale.** The relation of the gas scale with the **absolute scale** is discussed in Chap. XIII.

Fig. 6.—Beckmann Thermometer.

(*c*) **Platinum Resistance Thermometer.**

This thermometer is described in detail in Part V.
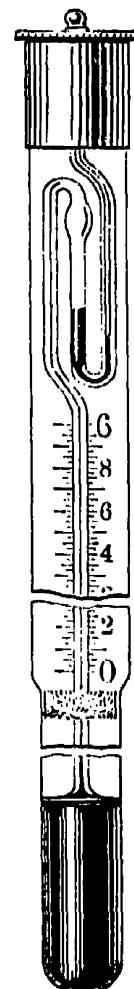
(*d*) Thermocouples.

These instruments are described in detail in Part V.

(*e*) Radiation Pyrometers.

The radiation pyrometers are instruments which depend for their action on the properties of Radiant Heat. They are therefore described in Chap. XIV. They are of two distinct types: (*a*) the *total radiation pyrometer* associated with Stefan's law, and (*b*) the *optical pyrometers* based on Planck's law.

(*f*) Vapour Pressure Thermometers.

These depend for their action on the variation of vapour pressure with temperature, which is discussed more fully in Chap. IX.

(*g*) Magnetic Susceptibility Thermometers.

The variation of the magnetic susceptibility (see Part V) with temperature has been used to measure temperatures near the absolute zero.

(*h*) Strain Thermometers.

These depend for their action on the unequal expansion of different materials for the same temperature rise. Two short bars of equal length but of different metals are placed side by side and attached rigidly to a metal cross-piece at one end. If the temperature is raised, one bar expands more than the other and a suitable system of levers may be actuated by the unequal expansion to move a pointer over a scale as in the " radiator " indicator attached to automobiles.

We conclude this chapter with a table stating some of the advantages and disadvantages of the various types of thermometer mentioned.

Type	Advantages	Disadvantages	Range
1. **Liquid in glass**	(1) Simple; (2) convenient size; (3) direct reading; (4) easy to read; (5) moderately quick in action.	(1) Restricted range; (2) zero changes with time owing to contraction of glass envelope: this reduced to a minimum by " aging " the glass naturally or artificially; (3) variation in reading with the length of the column exposed: correction can be calculated; (4) reading varies with changes in external and internal pressure: corrections obtained by calibration.	− 30° C. to 400° C. with nitrogen above mercury. 30° C. to −100° C. with alcohol.

Type	Advantages	Disadvantages	Range
2. Gas thermometer	(1) Enormous range; (2) no effective zero changes since expansion of envelope $\ll$ gas expansion; (3) accurate values owing to large gas expansion; (4) individual corrections not required since all permanent gases identical in behaviour.	(1) Complicated; (2) bulky; (3) slow in action; (4) uncertain corrections for the " dead space "; (5) not direct reading.	$-270°$ C. to $2500°$ C.
3. Platinum resistance thermometer	(1) Wide range; (2) no zero change; (3) reads easily to $1/50°$ C.; (4) quick reading.	(1) Complicated; (2) expensive; (3) not direct reading.	$-200°$ C. to $1200°$ C.
4. Thermocouples	(1) Wide range; (2) moderately cheap; (3) quick reading; (4) very low heat capacity and small size ensures minimum disturbance due to thermometer.	(1) Complicated; (2) requires frequent calibration as zero changes; (3) not direct reading.	$-270°$ C. to $2000°$ C.
5. Radiation Pyrometers (a) *Total radiation type*	(1) Large range; (2) otherwise as for thermocouples.	(1) Complicated; (2) requires calibration as T^4 law only applicable to black bodies (see Chap. XIV).	$500°$ C. upwards.
(b) *Optical type*	(1) Large range; (2) not so dependent as type (a) on black body conditions; (3) does not require such a large area of emitter as type (a).	(1) Complicated; (2) requires calibration as Planck's law is strictly true for black bodies only.	$600°$ C. upwards.
6 and 7. Vapour pressure thermometers and magnetic susceptibility thermometers	Useful at very low temperatures.	(1) Complicated; (2) require calibration against gas thermometer at higher temperatures and then have to be subjected to rather uncertain extrapolation down into the region where they are to be used.	$0°$ to $5°$ *absolute*.

EXERCISES

1. Explain clearly how a scale of temperature is established and discuss the choice of fixed points.

2. An accurate Fahrenheit thermometer and a Centigrade thermometer register 160° and 70° respectively when placed in the same enclosure, which is at uniform temperature.

What is the error in the Centigrade thermometer? [−1·1° C.]

3. Write a short essay on the methods of measuring temperature.

Thermal Expansion of Solids and Liquids

1. Introduction.

It is a matter of common observation that a change of size occurs when the temperature of a body is changed. In general the change is undesirable and allowances must be made for it. For example, railway lines are laid down in short lengths which are placed end to end but not quite in contact. Expansion consequent on rise of temperature does not then cause buckling of the rails. Similarly, long steam pipes are not made quite straight but have a loop or bend at intervals to provide " slack " which may be taken up or given out according as the temperature falls or rises.

2. Coefficients of Expansion.

When a rod is heated, its change in length is much larger than its change in breadth or depth. Considering only the change in length, we define the **coefficient of linear expansion** a of the material of the rod by the relation

$$a = \frac{l_t - l_0}{l_0 \, t}, \quad \cdots \cdots \cdots \quad (2.1)$$

where
$l_0 =$ length of rod at its initial temperature,
$l_t =$ length of rod when it has been raised t°,
$t^\circ =$ rise in temperature.

The coefficient of linear expansion is therefore the increase in length divided by the original length for a rise in temperature of 1°. Equation (2.1) is often written in the form

$$l_t = l_0(1 + at). \quad \cdots \cdots \cdots \quad (2.2)$$

Again, if a square plate as shown in fig. 1 is heated, the change in area is relatively larger than the change in thickness. If we concentrate

the change in area, we define the **coefficient of surface expansion** β a relation similar to (2.1),

$$\beta = \frac{S_t - S_0}{S_0 t}, \qquad \ldots \ldots \ldots \quad (2.3)$$

where
S_0 = area of plate at its initial temperature,
S_t = area of plate when it has been raised $t°$,
$t°$ = rise in temperature.

Equation (2.3) may alternatively be written

$$S_t = S_0(1 + \beta t). \qquad \ldots \ldots \ldots \quad (2.4)$$

Further, reference to fig. 1 shows that β and α are related, for $S_t = l_t^2$, so from equation (2.2)

$$S_t = l_0^2(1 + \alpha t)^2 = S_0(1 + 2\alpha t + \alpha^2 t^2)$$
$$= S_0(1 + 2\alpha t), \qquad \ldots \ldots \ldots \ldots \quad (2.5)$$

for $S_0 = l_0^2$, and we may neglect the term involving α^2 except for very large temperature changes since $\alpha \simeq 10^{-6}$ per °C. Hence, comparing equations (2.4) and (2.5), $\beta = 2\alpha$, or the coefficient of surface expansion is twice the coefficient of linear expansion. The relation is sufficiently true to make it quite unnecessary to measure the coefficient of surface expansion for a material if its coefficient of linear expansion has been already determined.

Fig. 1.—Expansion of Square Plate

Finally, if a cube is heated it expands, the coefficient of volume expansion γ being defined by

$$\gamma = \frac{V_t - V_0}{V_0 t}, \qquad \ldots \ldots \ldots \quad (2.6)$$

or, as it may be written,

$$V_t = V_0(1 + \gamma t). \qquad \ldots \ldots \ldots \quad (2.7)$$

It is left as an exercise to the student to show that $\gamma = 3\alpha$ approximately.

These simple relations between the coefficients of expansion hold only for isotropic substances (see Chap. VIII, Part I). Some crystals expand by different amounts along their different crystallographic axes.

3. Timepieces.

The time of oscillation of a pendulum is governed mainly by the distance of the centre of gravity of the pendulum from the axis of suspension. Consequently, when a rise in temperature occurs the clock loses, for the length of the pendulum is increased and therefore the time of oscillation also (see Chap. III, Part I). To allow for this, pendulums are often constructed of wood, the coefficient of expansion of which is exceptionally small. More robust pendulums are made of **invar steel,** a nickel steel alloy, which also has a very small coefficient of expansion. Unfortunately invar has a sufficiently high magnetic susceptibility to be influenced by changes in the earth's magnetic field. Other alloys, such as **elinvar,** are less influenced and therefore more suitable. Before the introduction of these alloys, methods of compensation had to be used. Thus **Harrison's grid-iron pendulum** consisted of alternate bars of iron and brass connected as shown in fig. 2. Change of temperature resulted in a lowering of the pendulum bob due to the expansion of the iron rods and a rise due to the expansion of the brass rods. Clearly the height of the bob will not change if $l_1\alpha_1 = l_2\alpha_2$, where l_1 and l_2 are the **total** lengths of iron and brass rods respectively, and α_1 and α_2 are the coefficients of linear expansion of the two metals.
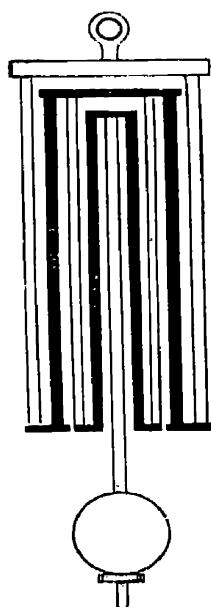

Fig. 2.—Harrison's Grid-iron Pendulum.
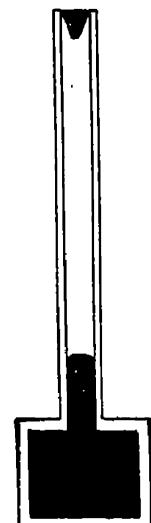
Fig. 3.—Graham's Hollow Iron Rod Pendulum.

An alternative pendulum designed by Graham consisted of a hollow iron rod as shown in fig. 3, attached to a reservoir containing mercury. Increase in length of the iron rod was compensated by a rise in the level of the mercury. By adjusting the quantity of mercury, exact compensation could be obtained.

In watches, the time is controlled by the **balance wheel,** the period of the oscillation of which is governed by the moment of inertia (see Chap. IV, Part I) of the wheel about its axis of oscillation. As the temperature rises the spokes of the wheel expand, the rim of the wheel is pushed farther from the axis and the moment of inertia is increased. The main contribution to the moment of inertia is from small screw-weights situated on the rim of the wheel, and if these are kept at a constant distance from the axis compensation is attained. Accordingly,
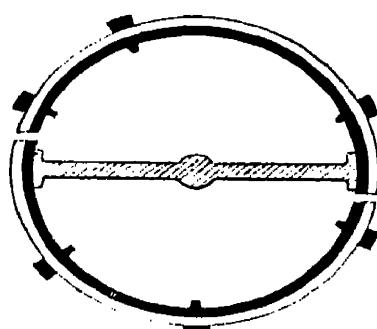
Fig. 4.—Balance Wheel

the rim of the wheel is made of two metals as shown in fig. 4, with different coefficients of expansion. The metal with the lower coefficient is placed on the inside and that with the larger coefficient on the outside. Consequently, when the temperature rises the curvature of the rim increases, and by suitable adjustment the amount by which the increased curvature of the rim brings the weights closer to the axis may be made exactly equal to the amount by which they are thrust outwards from the axis by the expansion of the spokes.

4. Useful Applications of Thermal Expansion.

Perhaps the most useful application of thermal expansion is the use of liquids as thermometric substances. Apart from this use, which we have already discussed in Chap. I, a number of other applications may be noted.

In former times, and to some extent to-day, cart-wheels are made of wood, bound by a steel hoop. The latter is fixed in position by heating the hoop until its internal diameter is sufficiently large to allow it to be slipped over the wheel. On cooling, the metal rim contracts and grips the wooden wheel firmly.

The S-shaped piece of iron seen on the outside of some farm-buildings is an indication of a tie-rod which runs through the rafters and is attached at each end to an S-shaped piece. The purpose is to strengthen the walls of the barn, and the arrangement is fixed in position by heating the rod in the centre and then screwing the S-shaped pieces as close as possible to the outside of the two opposite walls. When the tie-rod cools and contracts a large stress is set up tending to pull the two walls together and prevent outward collapse.

If it is desired to attach machine parts, such as a wheel and axle or gun barrels, without the use of set-screws, then the two parts may be " sweated " together by having the hole in the wheel slightly smaller than the diameter of the axle and then heating the former until it will slip over the axle. The method has the disadvantage that the metals may suffer by heat treatment. Accordingly, the more recent method of **shrinkage fits** is often used. For the example quoted above, the axle is immersed in " dry ice ", the trade name for solid carbon dioxide. The temperature of the axle is thus reduced to about $-80°$ C., and the axle contracts sufficiently to allow it to be inserted into the wheel.

We may also note that since platinum has approximately the same thermal coefficient of expansion as glass, platinum wires may be fused through holes in a glass vessel and no strain will occur when the whole returns to room temperature. It is also possible to fuse glass to other metals if the latter are made sufficiently thin so as to give easily and take the strain when the glass cools.

Another useful application of thermal expansion is the gas regulator and **thermostat.** One form of thermostat is shown in fig. 5. A

long bulb B is filled with toluene (a liquid of exceptionally large expansion coefficient) which is in contact with a mercury column. Gas entering by the tube T_1 proceeds to the burner by the main tube T_2. If the temperature in the neighbour-hood of B rises sufficiently, the toluene expands and pushes the mercury up the tube; the gas supply is thus cut off by the blocking of T_2. Actually a small bypass T_3 allows sufficient gas to pass to keep the flame burning, but the heat provided is insufficient to maintain the temperature of B. Consequently, the toluene contracts and more gas is again admitted through T_2. In this way the temperature in the neighbour-hood of B is maintained constant to one or two degrees. A simple modification of the apparatus uses electrical heating, the moving mercury column being used to make and break electrical contacts.

Fig. 5.—Thermostat

5. Measurement of Linear Expansion.

As the coefficient of linear expansion is very small, direct measurement with an ordinary scale is impossible. Various methods of magnification have therefore to be adopted. Mechanical and optical levers may be used, but the best methods are either comparator or interferometer methods.

(a) Comparator Methods.

In these methods the bar AB may rest freely on rollers as shown in fig. 6, the whole being enclosed in a double-walled box with glass
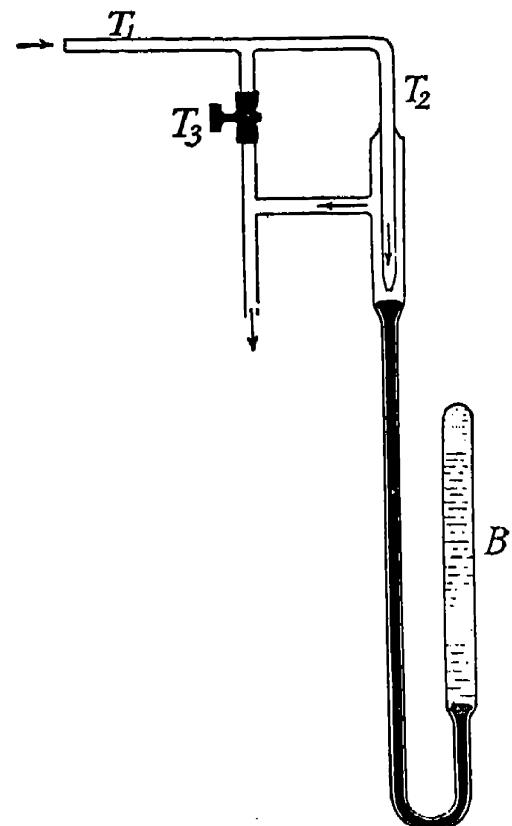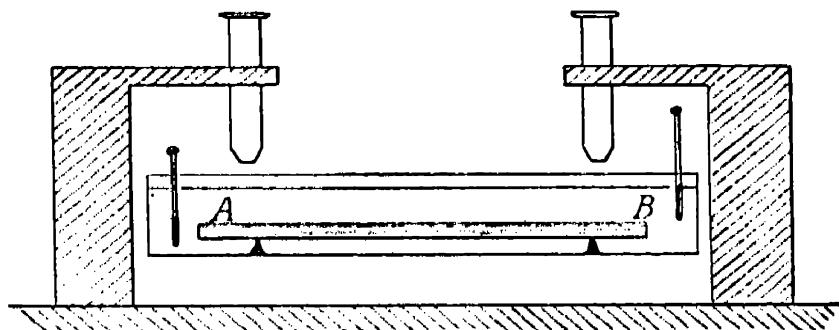
Fig. 6.—Measurement of Linear Expansion

windows through which two scratches on the bar may be observed with microscopes containing calibrated scales in the eye-pieces. Water is then allowed to surround the bar, the temperature being thermo-

statically controlled. The temperatures are read from thermometers inserted in the water-bath and the changes in length are read directly on the scales in the eye-pieces of the microscopes which are focussed on the scratches on the bar. If the changes in length are too large for the scratches to remain on the scale in the eye-piece, the whole microscope must be attached to a carriage which may be moved by a micrometer screw. In all circumstances the microscopes must be firmly mounted, preferably on stone pillars.

*(b) *Fizeau's Interference Methods for Crystals.*

The student will appreciate this method fully only after having grasped the contents of Chap. VII, Part III, Light. In fig. 7, a lens A is allowed to rest on three points above a polished metal table B, and the specimen C whose coefficient of expansion is required is inserted between A and B. A Newton's rings system is formed in the air-space between A and C and the temperature of the whole is then raised. Owing to the expansion of C, the thickness of the air-space changes, and this is accompanied by a movement in the Newton's rings system. In particular, rings appear to be born in the centre of the system and to expand outwards. Counting of the number of rings created allows changes in height of the specimen to be measured to 10^{-5} cm. Allowance must be made for the increased size of the apparatus as a whole and for the changes in refractive index of air when the temperature is changed. This is achieved by performing a subsidiary experiment without the specimen in position.

Fig. 7.—Fizeau's Interference Method

6. Forces produced by Change of Temperature.

The student should read the articles on stress and strain in Chap. VIII, Part I, before proceeding with this section.

(a) *Force required to hold a Heated Bar Extended.*

Suppose a bar is allowed to cool but is prevented from contracting by being gripped at the ends. Then if l_t is the free length at the higher temperature and l_0 is the free length at the lower temperature, the rod is being kept in a state of increased length $(l_t - l_0) = l_0 a t$ from equation (2.2). The tension P set up in the rod is therefore that which would be required to increase the rod from a length l_0 by an amount $l_0 a t$.

From the definitions of stress and of Young's Modulus of Elasticity q we have therefore

$$q = \frac{\text{stress}}{\text{strain}} = \frac{P/A}{l_0 a t / l_0},$$

or
$$P = qAat. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.8)$$

(b) Force required to prevent a Heated Bar from Extending.

The force required to prevent a bar extending when it is heated is clearly the force required to compress the rod back to its original length at the higher temperature after it has been freely allowed to expand. Hence

$$q = \frac{\text{stress}}{\text{strain}} = \frac{P/A}{l_0 a t / l_t} = \frac{P/A}{l_0 a t / l_0 (1 + at)},$$

or
$$P = \frac{qAat}{1 + at}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.9)$$

Since a is very small, the denominator of (2.9) is nearly unity so that (2.8) and (2.9) are in practice almost identical.

7. Cubical Expansion of Liquids.

Consideration of the thermal expansion of liquids leads to problems which do not occur with solids. For example, the liquid must be enclosed in a container, and in general the container will expand as well as the contained liquid, if a rise in temperature occurs. The apparent increase in volume which the liquid undergoes is therefore less than the true increase. Consequently, substitution in the expression (2.6)

$$\gamma = \frac{V_t - V_0}{V_0 t}$$

will only give an **apparent coefficient of expansion.** The true or **absolute coefficient of expansion** will be greater than this and we shall show immediately that

$$\gamma_{\text{absolute}} = \gamma_{\text{apparent}} + \gamma_{\text{container}}. \quad . \quad . \quad . \quad (2.10)$$

The thermal expansion of liquids differs from that of solids in at least two other ways. First, while a given solid expands by equal amounts over almost any part of the temperature scale, liquids expand at different rates in different temperature regions. Some liquids, such as water, **contract** when the temperature is raised a few degrees at certain parts of the temperature scale. With liquids, therefore, it is usual to define a **mean coefficient of expansion**

$$\gamma_m = \frac{V_t - V}{V t}, \quad . \quad . \quad . \quad . \quad . \quad (2.11)$$

where V is the volume at any temperature and V_t the volume of the same mass of liquid at a temperature $t°$ higher; and a **zero coefficient of expansion**

$$\gamma_0 = \frac{V_1 - V_0}{V_0}, \quad \dots \dots \quad (2.12)$$

where V_0 is the volume at $0°$ C. and V_1 the volume at $1°$ C.

Secondly, the thermal behaviour of liquids differs from that of solids in that their coefficient of cubical expansion is usually several hundred times larger than that of solids.

To deduce equation (2.10), we note the experimental fact that a hollow container such as a bottle expands just as though the bottle were solid.

Let V_0 = initial vol. of bottle at lower temp.; V_t = vol. of bottle when temp. is raised $t°$.

Then if the bottle contained a volume V_0 of the liquid at the lower temperature, suppose the observed volume of that liquid at the higher temperature is $V_{app.}$ and its true volume $V_{abs.}$. Then

$$V_{app.} = V_{abs.} - (V_t - V_0), \quad \dots \dots \quad (2.13)$$

since the expression in brackets represents the change in volume of the container. Applying equation (2.6),

$$\gamma_{app.} = \frac{V_{app.} - V_0}{V_0 t}, \quad \dots \dots \quad (2.14)$$

and

$$\gamma_{abs.} = \frac{V_{abs.} - V_0}{V_0 t}, \quad \dots \dots \quad (2.15)$$

Subtracting (2.14) from (2.15),

$$\gamma_{abs.} - \gamma_{app.} = \frac{V_{abs.} - V_{app.}}{V_0 t} = \frac{V_t - V_0}{V_0 t} = \gamma_{cont.},$$

from (2.13) and the definition of $\gamma_{cont.}$. This proves (2.10).

8. Variation of Density of Liquids with Temperature.

For a given mass m of liquid, from the definition of density (i Chap. IX, Part I),

$$m = \rho_0 V_0 = \rho_t V_t. \quad \dots \dots \quad (2.16$$

where ρ_0, ρ_t are the densities at $0°$ and $t°$, and V_0 and V_t the corresponding volumes at these two temperatures. Hence, substituting in (2.6),

$$\gamma = \frac{\dfrac{m}{\rho_t} - \dfrac{m}{\rho_0}}{\dfrac{m}{\rho_0} \cdot t} = \frac{\rho_0 - \rho_t}{\rho_t t}, \qquad \cdots \cdots \quad (2.17)$$

or alternatively

$$\rho_0 = \rho_t(1 + \gamma t). \qquad \cdots \cdots \cdots \quad (2.18)$$

9. Variation of Density of Water with Temperature.

The thermal behaviour of water is exceptional in that it contracts fairly uniformly from room temperature down to $4°$ C., after which,
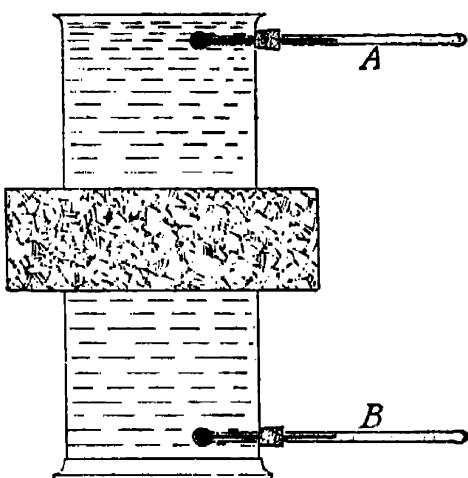
Fig. 8.—Hope's Apparatus for Density of Water
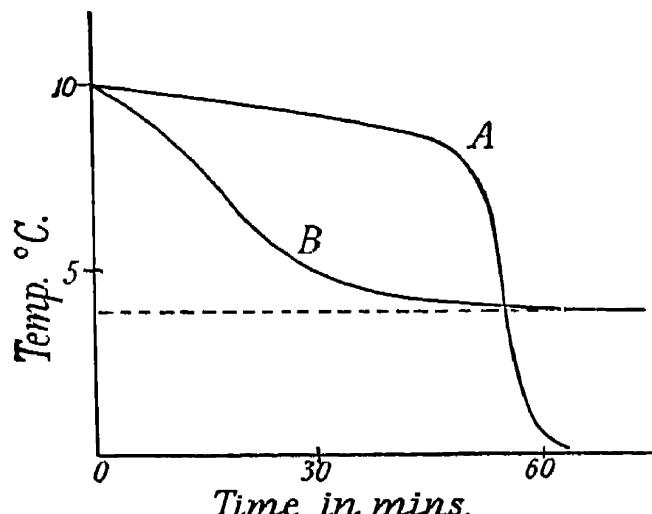
Fig. 9.—Temperature-time Curves

instead of continuing to contract it expands until it turns into ice at $0°$ C. The temperature $4°$ C. is said to be the temperature of the **maximum density of water,** and the existence of the phenomena is usually shown with an apparatus due to Hope. As shown in fig. 8, **Hope's apparatus** consists of a vertical hollow metal cylinder closed at the base, open at the top and surrounded round its centre by an annular tray. Pure water is placed in the cylinder and the temperature of the two thermometers A and B is observed to be the same. A freezing mixture is then introduced into the tray and temperature-time curves of A and B are then taken. The type of graph obtained is shown in fig. 9. The point where the two curves cross is the temperature of maximum density. The curves are explained as follows. As the layer of water at the centre of the cylinder is cooled by the mixture, its density is increased and consequently it sinks to the bottom of the cylinder. The temperature of the lower thermometer B therefore drops very rapidly, while that of the top thermometer A remains almost un-

changed except for a slight lowering due to cooling by the very small conduction through the water from the cold layer at the centre. When the temperature of the central layer falls below 4° C., however, the cold layer becomes less dense than the water below it: consequently it tends to rise and thus cools the water *above* the central layer. The top thermometer A is therefore affected and shows a rapid lowering of temperature. Since the cold layers become less and less dense as their temperature approaches 0° C., they rise to the surface and freezing occurs first on the top of the water. The water at the bottom
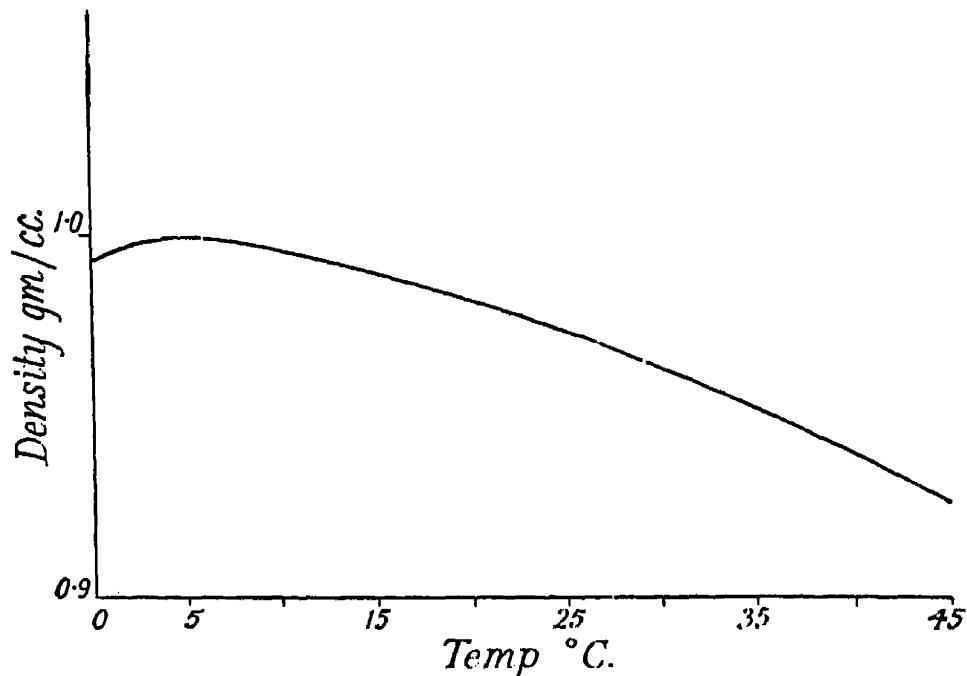
Fig. 10.—Density-temperature Graph of Water

of the vessel is still at a temperature of about 4° C. This behaviour is of great importance in nature, since it allows aquatic animals to exist at the bottom of the water in which they live. If the density of water continued to increase as the temperature fell to 0° C. the water would freeze from the bottom upwards and the organisms would be forced to the surface.

A graph of the variation of the density of water with temperature is shown in fig. 10. Note that the graph is not linear and the expansion is not uniform even after a temperature of 4° has been passed.

10. Measurement of the Thermal Expansion of Liquids.

(a) *Volume Method.*

By taking a flask with a long graduated neck and placing liquid inside it, the apparent coefficient of cubical expansion of the liquid can be found directly by immersing the flask in various temperature baths and noting the apparent volume of the liquid. The absolute coefficient of expansion of the liquid is then found by applying equation (2.10).

(b) Weight Thermometer.

In this method a bottle fitted with a perforated stopper (the weight thermometer) is first filled to the brim with liquid, weighed, and then heated through a known range of temperature. The liquid expands and some of it escapes from the bottle. The bottle is reweighed on cooling. Then if m_t and m_0 are the masses present at the higher and lower temperatures, and ρ_t, ρ_0, V_t, V_0 the corresponding densities and volumes respectively, then

$$V_0\rho_0 = m_0,$$
$$V_t\rho_t = m_t. \qquad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2.19)$$

Also, if γ is the coefficient of cubical expansion of the container,

$$V_t = V_0(1 + \gamma t), \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2.20)$$

while from (2.18)

$$\rho_0 = \rho_t(1 + \gamma_{\text{liq.}}t). \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2.21)$$

From (2.19), (2.20), and (2.21),

$$m_0/m_t = (1 + \gamma_{\text{liq.}}t)/(1 + \gamma t).$$

Hence
$$\gamma_{\text{liq.}} = \frac{m_0 - m_t}{m_t t} + \frac{m_0}{m_t}\gamma. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2.22)$$

Since the weight of a liquid may be determined with much greater accuracy than the volume, this method is superior to the previous one. However, it is not suitable for volatile liquids.

(c) Method based on Archimedes' Principle.

This method is a direct application of Archimedes' principle, and the experimental arrangement is that described in Part I, Chap. IX. For accurate results, a quartz cube whose expansion is negligible is suspended from one arm of a balance and dips into a vessel containing the liquid whose expansion coefficient is required. Then, as is shown in Part I, Chap. IX, the density of the liquid at any temperature may be obtained from a knowledge of the weight of the quartz cube in air and in the liquid respectively. To obtain absolute values of density, the volume of the cube must be known or some liquid of known density must be used to calibrate the instrument. If a sinker other than a quartz cube is used, allowance must be made for the increase in volume of the sinker as the temperature is raised.

(d) Absolute Methods: Regnault's Apparatus.

Dulong and Petit devised an elegant hydrostatic method which measures the absolute coefficient of expansion of a liquid without

allowance being required for the expansion of the container. The liquid was introduced into a vertical U-tube, one arm of which was surrounded by a bath at constant temperature, the other arm being in a bath of variable temperature. When the two arms are at different temperatures the liquid is in equilibrium only if the column is higher in the arm at the higher temperature. This is because the density of the hot liquid is less than that of the cold. The condition for equilibrium is clearly that the hydrostatic pressure at the bottom of the U-tube shall be the same in both directions, from the left and from the right; that is,

$$h_t\rho_t g = h_0\rho_0 g, \qquad (2.23)$$

where h_t and h_0 are the two heights respectively. Combining equation (2.23) with equation (2.18), we eliminate the densities and obtain

$$\gamma = \frac{h_t - h_0}{h_0 t}. \qquad (2.24)$$

The simple arrangement of Dulong and Petit is not quite satisfactory, since (1) a continuous circulation of hot and cold liquid takes place along the bottom of the U-tube, and (2) the quantity $(h_t - h_0)$ can be measured accurately only if the two levels are close together, and this is difficult to realize experimentally if they are to be maintained at different temperatures. Regnault therefore modified the original arrangement. His apparatus (fig. 11) consists of two wide vertical arms AB, CD, connected at the top by a narrow horizontal arm AC. At the base, AB and CD are each attached to a narrow horizontal tube which terminates in a narrow inverted U-tube from the top-end of which a tube leads to a compression air-pump. The liquid is then
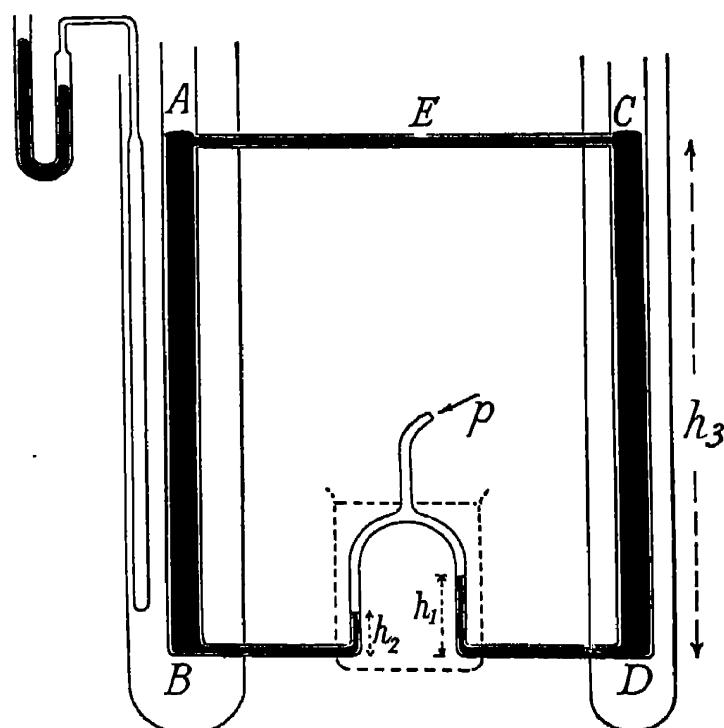

Fig. 11.—Regnault's Apparatus for Expansion of a Liquid

poured into AB and eventually fills AB and CD, but is prevented from rising too far in the Ω-tube by the compressed air. A small hole at E, open to the atmosphere, allows the top of the liquid to attain atmospheric pressure. The arm AB is then surrounded by a temperature bath, the other three arms all being at room temperature. If

h_1, h_2 and h_3 are the heights shown in fig. 11, then the condition for equilibrium at the bottom of AB and CD is given by

$$h_3\rho_0 g = p + h_1\rho_0 g, \qquad \ldots \ldots \quad (2.25)$$

$$h_3\rho_t g = p + h_2\rho_0 g, \qquad \ldots \ldots \quad (2.26)$$

where p is the air pressure in the Ω-tube.

Subtracting (2.25) and (2.26) and combining with (2.18), thus eliminating the densities, we obtain

$$\gamma = \frac{h_1 - h_2}{(h_3 - h_1 + h_2)t}. \qquad \ldots \ldots \quad (2.27)$$

The quantity $(h_1 - h_2)$ can be measured very accurately since the columns are at the same temperature and may be placed close together. The dimensions of Regnault's apparatus were 1 to 2 m. The effect has been magnified by later workers, particularly Callendar and Moss, by using six columns in series, each 2 m. long, but the principle remains the same.

EXERCISES

1. Define *coefficient of thermal expansion*. In what units may it be expressed?
Show that the coefficient of cubical expansion of a homogeneous solid is approximately three times its coefficient of linear expansion.

2. Describe an *accurate* method for measuring the coefficient of linear expansion of a rod.
Find the rise in temperature necessary to cause a pendulum clock to lose 1 sec. per day if the pendulum is made of brass of coefficient of linear expansion $1\cdot89 \times 10^{-5}$ per °C. [$1\cdot2$° C.]

3. Explain how clocks and watches are compensated for the thermal expansion resulting from temperature change.
What useful applications have been made of thermal expansion?

4. Show that provided the temperature change is not too large the force required to hold a heated bar extended, if it is allowed to cool from t_2° to t_1°, is approximately equal to the force such a rod would exert on rigid abutments if it is raised in temperature from t_1° to t_2°.

5. Enumerate methods for measuring the coefficient of cubical expansion of liquids, and describe in detail the method which you consider to be the best.

6. Show that the absolute coefficient of cubical expansion of a liquid is the sum of its apparent coefficient of expansion and the coefficient of cubical expansion of the material of the container.
Describe Regnault's method for measuring the absolute coefficient of expansion directly.

7. Describe how the variation of the density of a liquid with temperature may be determined.

A body floats in water at 4° C. and has 98 per cent of its volume immersed in the water. Determine the temperature of the water in which the body will be completely submerged, given that the mean coefficient of cubical expansion of water is to be taken as $2 \cdot 5 \times 10^{-4}$ per °C. and the expansion of the body may be neglected. [85·6° C.]

8. Describe Hope's apparatus for demonstrating the variation of the density of water with temperature and discuss the results as fully as possible.

9. Explain carefully the construction and use of a weight thermometer, deducing any formulæ which you may consider necessary.

A glass weight thermometer is just filled with 15 c.c. of mercury at 15° C. If the coefficient of cubical expansion of mercury is $1 \cdot 82 \times 10^{-4}$ per °C., and the coefficient of linear expansion of glass is $9 \cdot 00 \times 10^{-6}$ per °C., find the weight of mercury which escapes when the temperature is raised to 100° C., given that the density of mercury at 15° C. is 13·56 gm./c.c. [2·64 gm.]

10. The two arms of a vertical U-tube are at 0° C. and 100° C. respectively, and the difference in the height of the two columns of an enclosed liquid is 1·50 cm. If the cooler column is 60 cm. high, find the coefficient of cubical expansion of the contained liquid. [$2 \cdot 5 \times 10^{-4}$ per °C.]

CHAPTER III

Quantity of Heat

1. Introduction.

If we mix a given mass of water at, say, 60° C. with the same mass of water at 40° C. we shall find that the temperature of the mixture is 50° C. If, however, we take the same mass of some other substance, such as copper, at 60° C., and place it in the same mass of water at 40° C. we shall find that the temperature of the mixture is only about 42° C. We explain this by stating that the copper contained much less heat than the same mass of water. The quantity of heat H lost or gained by a substance is found to be proportional to the weight, the temperature change θ which it undergoes and the nature of the substance, that is,

$$H = ms\theta, \qquad \ldots \ldots \ldots \quad (3.1)$$

where s is a constant depending on the nature of the substance and is termed its **specific heat.** The specific heat of water is defined as unity, and the *unit quantity of heat* is obtained from (3.1) by putting $m = s = \theta = 1$. On the C.G.S. system therefore **the unit of heat or calorie is the amount of heat required to raise 1 gm. of water through 1° C.** Very accurate measurements show that the quantity of heat is not the same for different parts of the temperature scale. Consequently, for accurate work we must either specify the **mean calorie,** which is the average amount of heat per °C. over the temperature range considered, or else specify some definite temperature. Thus the **15° C. calorie** is the amount of heat required to raise 1 gm. of water from 14·5° C. to 15·5° C.

The calorie is a small quantity of heat, and for industrial purposes the **major calorie** is often used. This is defined to be 1000 times the ordinary calorie. On the F.P.S. system $m = 1$ lb. and $\theta = 1°$ C. or 1° F. Hence we have also as units of quantity of heat *the lb.* $-°C.$ *and the lb.* $-°F.$, *the amounts of heat required to raise 1 lb. of water through 1° C. or 1° F. respectively.*

2. Specific Heat.

Let us suppose that a given mass of water requires a quantity of heat H_1 to raise its temperature by θ, and that the same mass of some

other material requires an amount of heat H_2 for the same temperature range. Then, applying equation (3.1),

$$H_1 = m \times 1 \times \theta$$

and

$$H_2 = m \times s \times \theta. \qquad \cdots \cdots \cdots \cdot (3.2)$$

Hence $s = H_2/H_1$ or the *specific heat of a substance is the ratio of the amount of heat required to raise the temperature of a given mass of the substance through a given temperature range to the amount of heat required to raise the same mass of water through the same temperature range.* Defined in this way, specific heat is a dimensionless quantity (see Part I, Chap. V). Alternatively, we may determine the dimensions from equation (3.1) alone, defining H and θ as new primary quantities, whereupon s has the dimensions $HM^{-1}\theta^{-1}$.

The product ms of equation (3.1) is often referred to as the **thermal capacity** or **water equivalent** of a body, since it gives the weight of water with the same thermal capacity as the given body. For example, the specific heat of copper is about $0 \cdot 1$: consequently the thermal capacity or water equivalent of 10 gm. of copper is $10 \times 0 \cdot 1 = 1$, and therefore 1 gm. of water is thermally equal to 10 gm. of copper.

3. Conservation of Heat.

When a body cools, the neighbouring bodies are observed to show a slight rise in temperature. It is therefore reasonable to assume that the heat lost by the cooling body is equal to the heat gained by those which are warmed. The quantity of heat present is therefore conserved and, in fact, as we shall see more clearly in Chap. VI, the Conservation of Heat is merely one particular case of the Conservation of Energy, since Heat and Energy are equivalent. The conservation of heat forms the basis of the methods for measuring specific heats.

There are four main methods for determining specific heats. These are:

(a) *Method of mixtures.*
(b) *Method of cooling.*
(c) *Electrical methods.*
(d) *Methods depending on latent heat.*

We discuss the first three methods in this chapter: examples of the last method are given in Chap. VI and VIII.

4. Method of Mixtures.

To determine the specific heat of an insoluble solid by the method of mixtures, a piece of the material M is attached to threads and is placed in a steam bath or **hypsometer**, as shown on the left in fig. 1, and allowed to take up the temperature of the steam. It is then dropped

very quickly through a trap-door T into a copper vessel containing water. This vessel is placed in a larger vessel, though it is prevented from coming in contact with it by a layer of cotton-wool. Such an arrangement constitutes a simple form of **calorimeter**, and is shown on the right in fig. 1. The temperatures of the water in the calorimeter are noted with a thermometer inserted in the water, before and after the introduction of the specimen, stirring being effected with a small copper stirrer. Then if

w = mass of calorimeter,

m = mass of water in calorimeter,

θ_0 = initial temperature of water and calorimeter,

θ_f = final temperature of water and calorimeter,

s = specific heat of material (usually copper) of calorimeter;
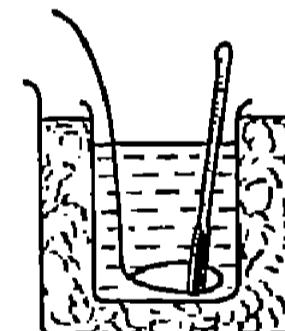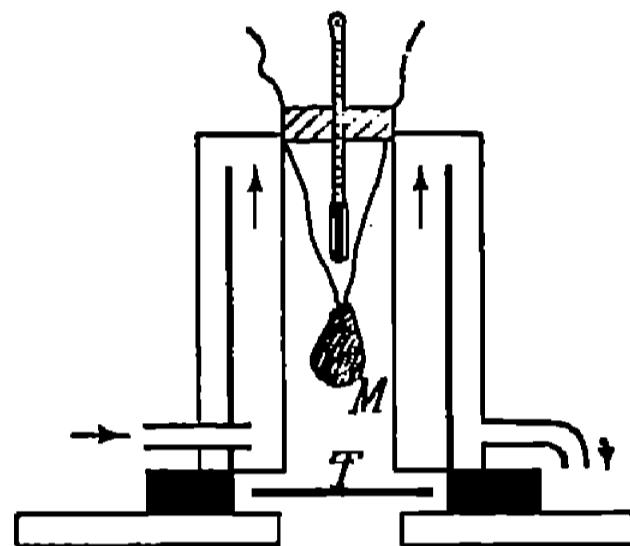
Fig. 1.—Hypsometer and Calorimeter

the heat gained by the water and calorimeter, when the specimen is dropped in, is by (3.1)

$$w \times s \times (\theta_f - \theta_0) + m \times 1 \times (\theta_f - \theta_0) = (\theta_f - \theta_0)(ws + m). \quad (3.3)$$

Now the heat lost by the specimen if its mass is M, its initial temperature θ_1 and its specific heat S, will be

$$MS(\theta_1 - \theta_f), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.4)$$

since its final temperature is that of the water and calorimeter. By the conservation of heat, (3.3) must equal (3.4); hence

$$MS(\theta_1 - \theta_f) = (\theta_f - \theta_0)(ws + m), \quad . \quad . \quad . \quad (3.5)$$

an equation by which, if the specific heat of the material of the calorimeter is known, S may be determined.

To find s for the calorimeter itself, a quantity of hot water at a known temperature is poured into the calorimeter containing cold water. It is left as an exercise to the reader to show that

$$s = \frac{M\theta_1 + m\theta_0 - (M + m)\theta_f}{w(\theta_f - \theta_0)}, \quad . \quad . \quad . \quad (3.6)$$

where m, w, θ_0, θ_1 and θ_f have the same significance as before and M is the mass of *hot* water poured into the calorimeter.

The validity of equation (3.5) depends on the assumption that *all* the heat lost from the hot body is eventually acquired by the water and the calorimeter. This is clearly not the case, for the cotton-wool surrounding the calorimeter will also have its temperature raised slightly. In fact, heat will be lost from the system by conduction through the cotton-wool, by convection of the air above the calorimeter and by radiation from the system as a whole. To appreciate these points fully the student should refer to Chap. IV and to a text-book of Practical Physics. We content ourselves here with noting that it is usually sufficient to apply corrections for

(1) heat capacity of thermometer and stirrer,
(2) heat lost by radiation and convection.

The heat capacity of the stirrer is known since it is usually made of copper: the heat capacity of the thermometer is found by taking a very small calorimeter containing warm water, the temperature of which as registered by an inserted thermometer A is, say, 30° C. The thermometer B, whose heat capacity is required, and which is reading room-temperature, is then inserted into the calorimeter immediately after the withdrawal of the thermometer A. Then since heat will have been required to raise thermometer B from room temperature to that of the water, it will register a temperature somewhat less than 30° C. Applying the equation, heat lost = heat gained, the water equivalent of thermometer B is obtained.

Heat is lost by radiation and convection during the time taken for thermal equilibrium to be reached after the specimen has been introduced into the calorimeter. For example, it may take over a minute before the temperature rises to its final steady value θ_f. During this time, heat is being lost from the system to the room and hence θ_f is smaller than it would otherwise be. To correct for this, a **cooling curve** is plotted, that is, the temperature of the whole system is raised until it is some 5° above θ_f; it is then allowed to cool by radiation and convection and a cooling curve or graph of temperature-time is constructed. This curve passes through θ_f, and the rate of cooling in degrees per minute is obtained directly by drawing a tangent to the cooling

curve at this temperature. Now the *average* rate of cooling during the main experiment was

$$\tfrac{1}{2}(\text{rate of cooling at } \theta_f + \text{rate of cooling at } \theta_0).$$

If θ_0 is room temperature, the rate of cooling at this temperature is zero. Consequently, the correction to be added to θ_f is

$$\delta\theta_f = \tfrac{1}{2}\ (\text{rate of cooling at } \theta_f) \times \text{time taken for temperature to rise from } \theta_0 \text{ to } \theta_f \text{ in main experiment.}$$

The above treatment of the heat loss is only approximate: for more accurate methods the student should consult a textbook of Practical Physics. The radiation and convection correction is smaller the smaller the difference between θ_0 and θ_f. While a small temperature rise is therefore desirable, the limited sensitivity of the thermometer makes a very small rise difficult to measure accurately. If the water in the calorimeter was initially as much below room temperature as it was finally above it, no radiation and convection correction is necessary. This method was introduced by Rumford: it holds only over a small temperature range.

5. Method of Cooling.

The specific heat of a solid soluble in water may be found by using in the calorimeter some liquid in which it is insoluble (cf. *Determination of Densities*, Part I, Chap. IX). The specific heats of liquids are easily found by pouring the warmed liquid into a copper calorimeter either empty or containing some of the liquid already but at a lower temperature. Another method known as the **method of cooling** is, however, particularly applicable to liquids. The apparatus consists of two small aluminium calorimeters, equal in all respects and carried at their top edge by ebonite bushes. Equal *volumes* of water and of the liquid whose specific heat is required are introduced into the two calorimeters, and each is fitted with a cork and a thermometer. Both calorimeters are raised some degrees above room temperature by immersion in a water-bath. They are then removed and placed in a draught-free enclosure as shown in fig. 2. If

$$m = \text{mass of water,}$$
$$s(=1) = \text{specific heat of water,}$$
$$m' = \text{mass of liquid,}$$
$$s' = \text{specific heat of liquid,}$$

and $t, t' = $ times taken for water and liquid to cool through the same temperature range respectively,

then

$$\frac{ms}{m's'} = \frac{t}{t'}. \qquad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3.7)$$

To prove (3.7), let dQ be the heat lost, per unit area, from the surface of the first calorimeter in a short time dt. Then if the area of the surface is A, and the dependence of heat loss on temperature is represented by some unknown function $f(\theta)$,

$$dQ = A\,f(\theta)\,dt. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3.8)$$

The temperature at time $t + dt$ is $\theta + d\theta$. Here $d\theta$ is negative, and hence, if the mass of the water is m,

$$dQ = -m\,s\,d\theta. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3.9)$$
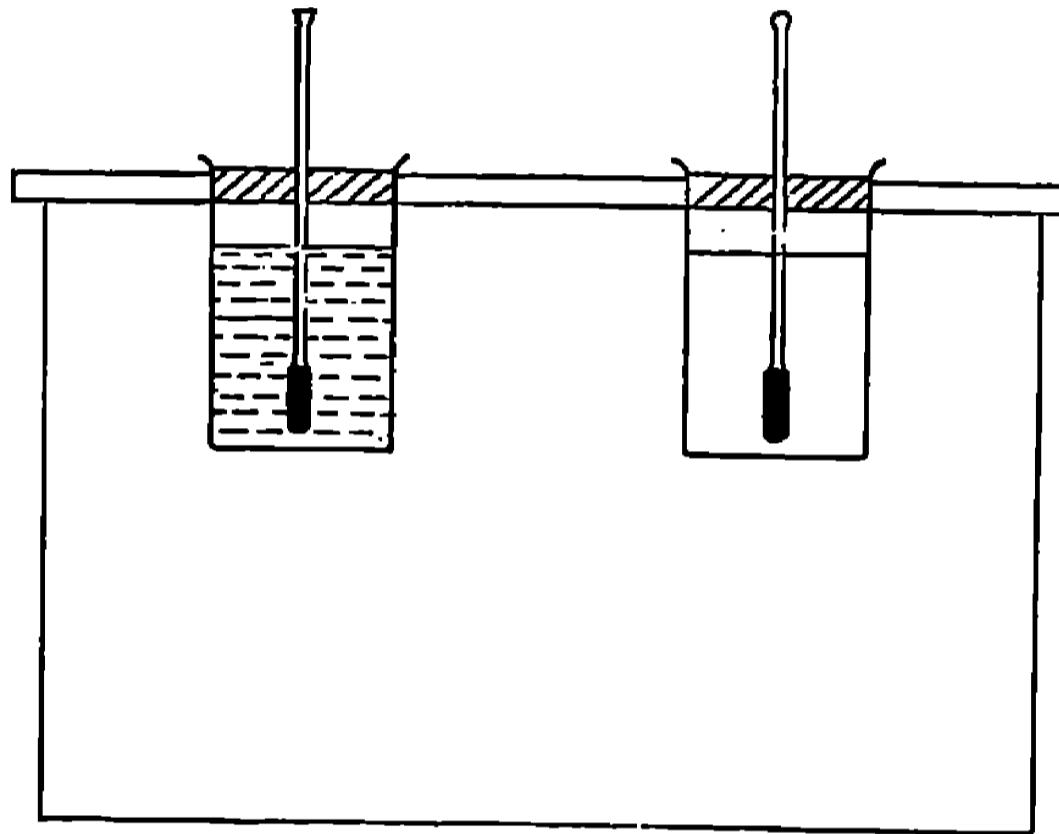
Fig. 2.—Method of Cooling

From (3.8) and (3.9)

$$dt = -\frac{ms}{A}\frac{d\theta}{f(\theta)}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3.10)$$

Integrating (3.10) and writing $F(\theta)$ for the temperature integral, we obtain

$$t = -\frac{ms}{A}F(\theta). \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3.11)$$

Now, since the calorimeters are identical, A is the same for the liquid as for the water; also the temperature ranges are equal, so $F(\theta)$ is the same. Hence, by analogy with (3.11),

$$t' = -\frac{m's'}{A}F(\theta), \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3.12)$$

and dividing (3.11) and (3.12) we obtain (3.7).

Equation (3.7) should strictly be written

$$\frac{ms + W}{m's' + W} = \frac{t}{t'},$$

where W is the water equivalent of either of the aluminium calorimeters. As these are very light and aluminium has a low specific heat, W is usually much less than ms or $m's'$. The method of cooling has the advantage that it involves no mixing and is suitable though only small quantities of the liquid are available.

6. Method of Electrical Heating.

This method is applicable to solids, liquids and gases, and is based simply on equation (3.1). A measured quantity of electrical energy is converted into heat H and the rise in temperature of a known mass of material is observed. We shall concentrate on its application to liquids as the apparatus is the simplest in this case. With liquids the electrical method is applied in two distinct forms:

(a) Joule's Method.

In this method, a coil of wire is inserted into a given mass of the liquid contained in a calorimeter, and a known amount of electrical energy is supplied. If

$m =$ mass of liquid present,
$s =$ specific heat of liquid,
$w =$ water equivalent of calorimeter,
$R =$ heat loss due to radiation and convection,
$t =$ time of passage of current,
$I =$ mean current,
$E =$ mean potential difference,
$J =$ Joule's Equivalent of Heat (see Chap. VI),
$\theta =$ rise in temperature,

then
$$H = \frac{EIt}{J} = (ms + w)\theta + R. \qquad \qquad (3.13)$$

The quantity R may be allowed for by plotting a cooling curve as described on pp. 28, 29. However, it is usually eliminated by repeating the experiment with a potential difference E' and current I', for a different mass of liquid m' but for the same time t over the same temperature range θ. The heat loss R' is therefore approximately equal to R, and rewriting (3.13) for the second experiment and subtracting the two equations, we find:

$$\frac{t(EI - E'I')}{J} = (m - m')s\theta. \qquad \qquad (3.14)$$

We note that the water equivalent of the calorimeter has also been eliminated. The method is very accurate and may be used to measure J, the mechanical equivalent of heat, as described on p. 54.

(b) Continuous Flow Method.

This method was introduced by Callendar and Barnes and was shown by them to be susceptible of a high degree of accuracy. As shown in fig. 3, the apparatus consists of a narrow glass or quartz capillary tube, down the centre of which is placed a fine platinum wire which is electrically heated. The liquid is flowing continuously down the tube and the temperatures of entrance and exit, θ_1 and θ_2, are recorded. The temperature θ_2 becomes steady when the liquid carries the heat away as fast as it is generated by the electric current.
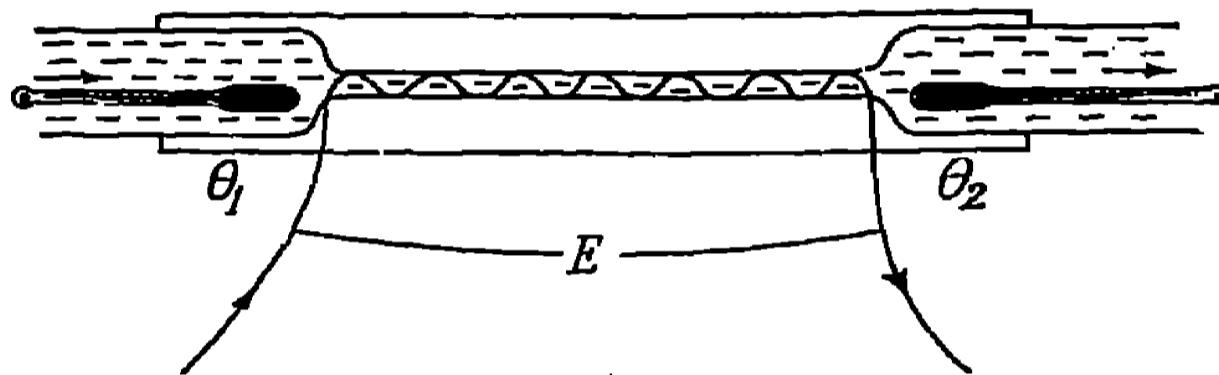
Fig. 3.—Continuous Flow Method of Callendar and Barnes

In this condition, which must be absolutely steady for accurate results,

$$H = \frac{EIt}{J} = ms(\theta_2 - \theta_1) + R, \quad . \quad . \quad . \quad (3.15)$$

where m = total mass of liquid flowing along tube in time t,

s = specific heat of liquid,

E, I = average values of potential difference and current during the experiment,

J = Joule's equivalent of heat,

R = heat losses due to radiation and convection.

As in the previous electrical method, to eliminate R, the experiment is repeated with different values of E, I and m but with the same values of t and $(\theta_2 - \theta_1)$. Subtraction gives the equation for s, free from corrections. Heat losses are much reduced by surrounding the flow tube with an exhausted tube or vacuum jacket. Platinum resistance thermometers or thermocouples are used in accurate work, rather than mercury thermometers as shown in fig. 3.

7. Variation of Specific Heat with Temperature.

By means of the continuous flow method it may be shown, by taking different ranges of temperature for $(\theta_2 - \theta_1)$, that the specific heat of water varies with its temperature. If the specific heat is plotted

as a function of the temperature, a minimum is observed at about 37° C. as shown in fig. 4. The liquid state is still not well understood and satisfactory explanations are likely to be complicated. Change of state affects the specific heat profoundly; for example, ice has a specific
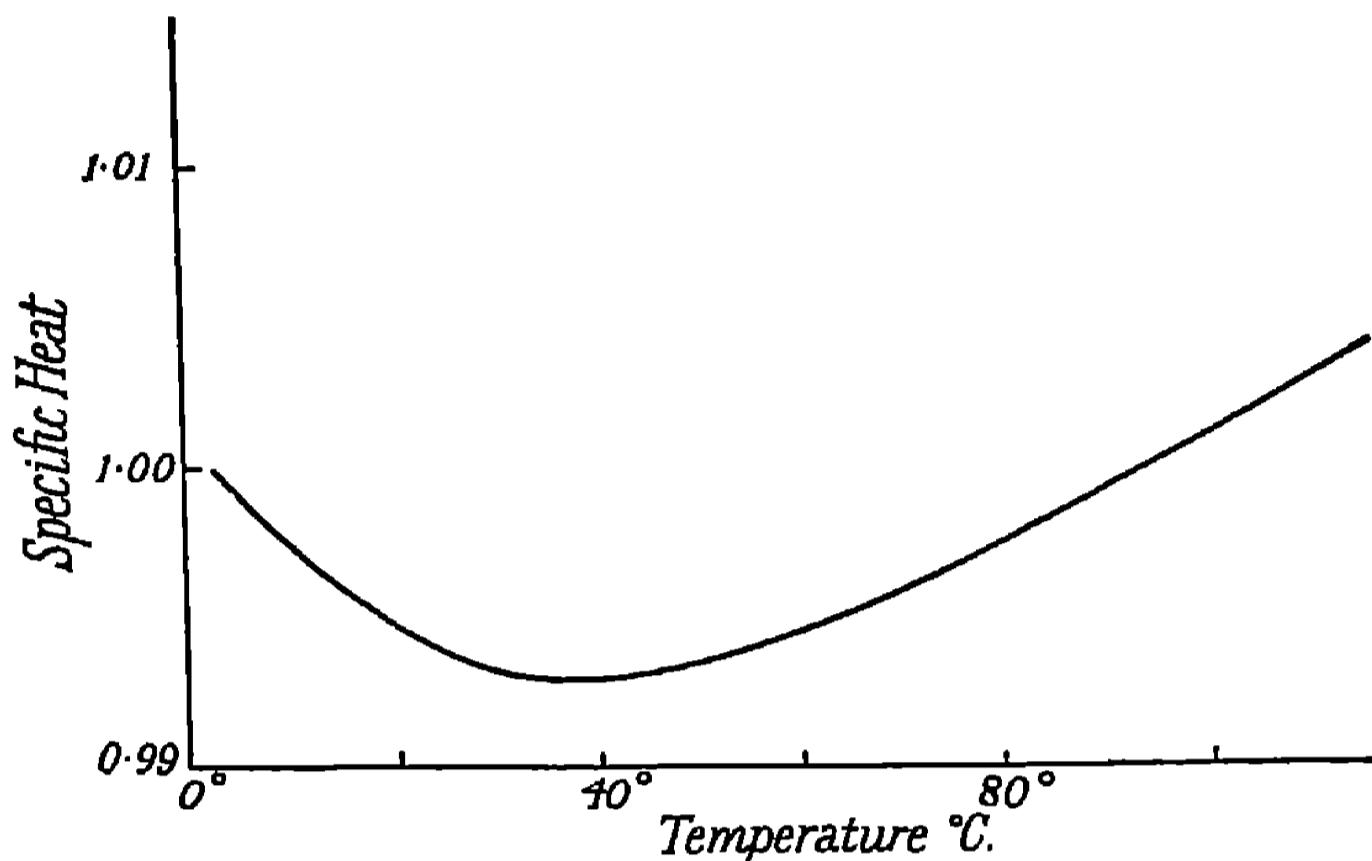

Fig. 4.—Temperature Variation of Specific Heat of Water

heat of about 0·5. At room temperature, many solids have an approximately constant specific heat over a moderate temperature range. At low temperatures, however, all show a marked decrease in the specific heat. In fig. 5, the atomic heats of some elements are plotted against the temperature (atomic heat = atomic weight multiplied by specific heat). The following points are of especial interest:
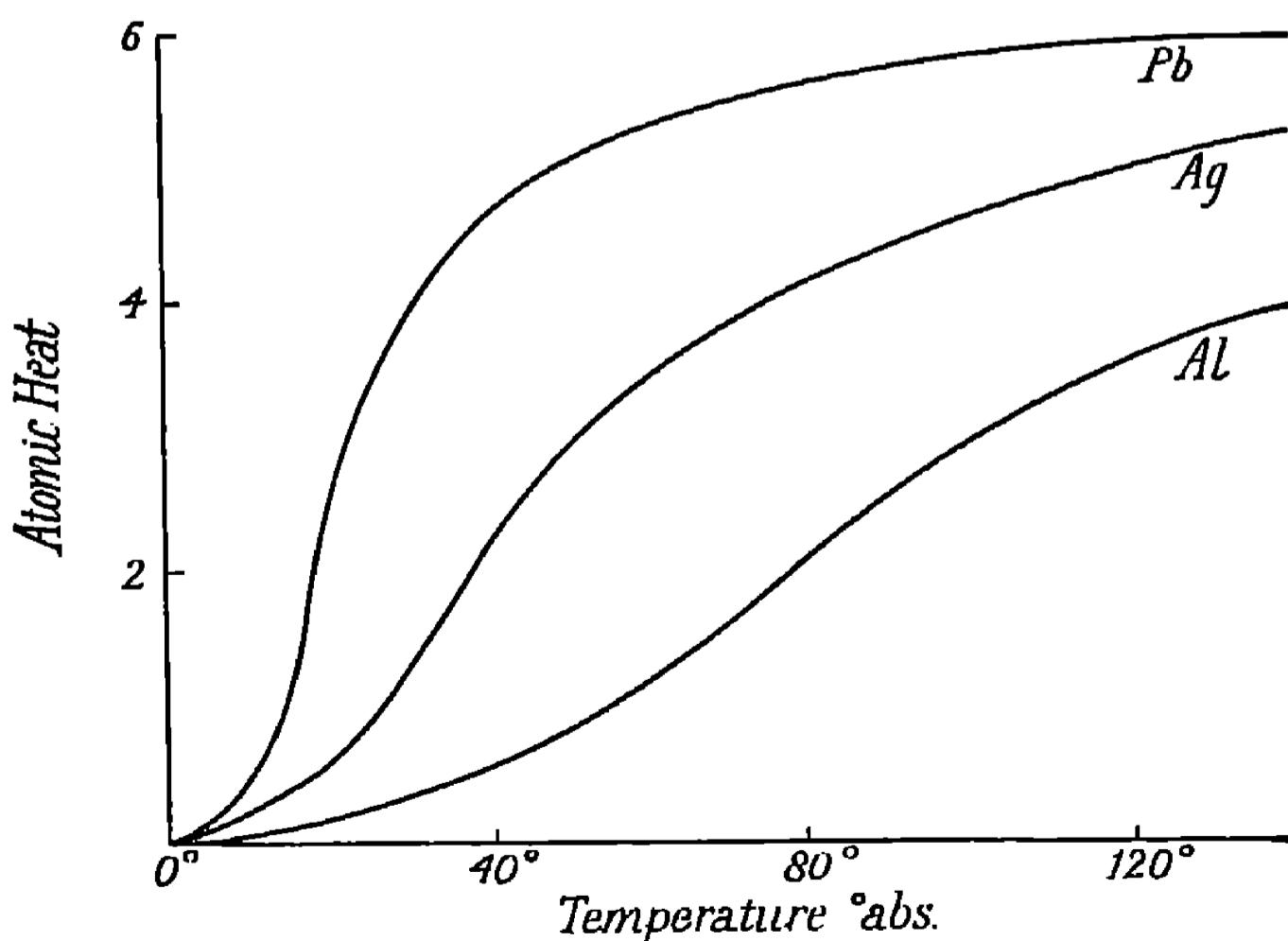
Fig. 5.—Atomic Heats of Aluminium, Silver and Lead

(i) Most elements approach the value 6·4 for their atomic heat at higher temperatures. This is **Dulong and Petit's law,** and was used in former times to determine the atomic weights of rare elements.

(ii) Elements which occur in different allotropic forms, such as gas carbon and diamond, have different specific heats, even at room temperature.

(iii) Metalloids have atomic heats considerably less than 6·4, even at room temperature.

(iv) At low temperatures, the atomic heats obey **Debye's law** which states that they are proportional to the cube of the absolute temperature.

EXERCISES

1. Define (a) *specific heat*, (b) *the calorie.*
How does the specific heat of a salt solution vary with the concentration, and how would you measure the variation experimentally?

2. Describe in detail the method of mixtures for finding the specific heats of substances, indicating clearly how corrections are applied for heat losses.

3. By what methods may the specific heat of liquids be determined?
Describe in detail the method of cooling, and find the specific heat of a liquid which has a mean density 3 gm./c.c., and which takes twice as long as an equal volume of water to cool through the same temperature range. [2/3.]

4. How have electrical methods been applied to determine the specific heats of liquids?
Find the percentage heat loss in a continuous flow experiment if 216 gm. of the liquid pass in 1 min., and show a steady rise in temperature of 1° C. when the current through the wire is maintained at 2 amp. and the potential across it at 4·2 volts. Joule's equivalent may be taken as 4·2 joules/cal., and the specific heat of the liquid as 0·5. [10 per cent.]

5. How may the water equivalent of a thermometer be determined?
What advantage has a thermocouple over a mercury thermometer in the measurement of temperature?

6. Describe suitable methods for finding the specific heat of (a) solids soluble in water, (b) strongly corrosive liquids like nitric acid.
What do you know of the variation of the specific heat of solids with temperature?

CHAPTER IV

Heat Transference and Convection

1. Introduction.

When a body cools it loses heat, or heat transference takes place, by three distinct processes, conduction, convection and radiation. We shall discuss convection in detail in this chapter, conduction and radiation being dealt with in Chap. V and XIV respectively.

If, for example, a hot piece of metal is laid on a wooden bench, heat is lost in the following manner. Conduction takes place where the metal is in contact with the wood and to a very small extent through the air. Radiation would take place even if the metal was suspended inside a vacuum. The main loss of heat, however, in the example considered is due to convection. It is important that the student should realize that conduction and radiation are essentially atomic and molecular phenomena, whereas convection is due to streaming of comparatively large masses of fluid. In fact, convection is confined to fluids, although conduction and radiation occur with both solids and fluids.

2. Convection.

The layer of air immediately above the metal in the above example is heated by conduction and radiation. Consequently, its density is decreased (see Chap. VII) and it rises, its place being taken by cold air which comes in at the sides. This cold air is in its turn warmed by the metal, its density is decreased and it rises also, and so the whole process is repeated until the metal is cooled to air temperature.

Such convection is termed *natural convection*, and is due to the fact that at the same pressure equal volumes of air have different densities at different temperatures. If a fan is used to circulate the air, cooling is due to *forced convection*.

3. Convection in Gases.

We may demonstrate convection in gases by the simple apparatus shown in fig. 1. A lighted candle is placed at the bottom of the opening in a bell-jar and it is found that after a short time the flame is extinguished. This is because the products of combustion are heavier than air; consequently they collect at the bottom of the jar and extinguish

the flame. For burning to continue indefinitely there must be a continual supply of fresh air. This is easily achieved by inserting a divider in the neck of the jar. If the candle is slightly to one side of the opening, the hot air rises out of the division above it and the heavier, cold fresh air passes down on the opposite side. That such a circulation is taking place may be shown by placing a small piece of smouldering rag near the down current of air. The smoke from the rag is carried down, thus showing visibly the direction of the air current.

Convection plays an important part in the **ventilation** of rooms. Hot air is continually passing up the chimney above a coal-fire and fresh cold air passes in under the door or at the windows.

On a large scale, convection is basically responsible for the **systems of winds.** Of these we shall consider:
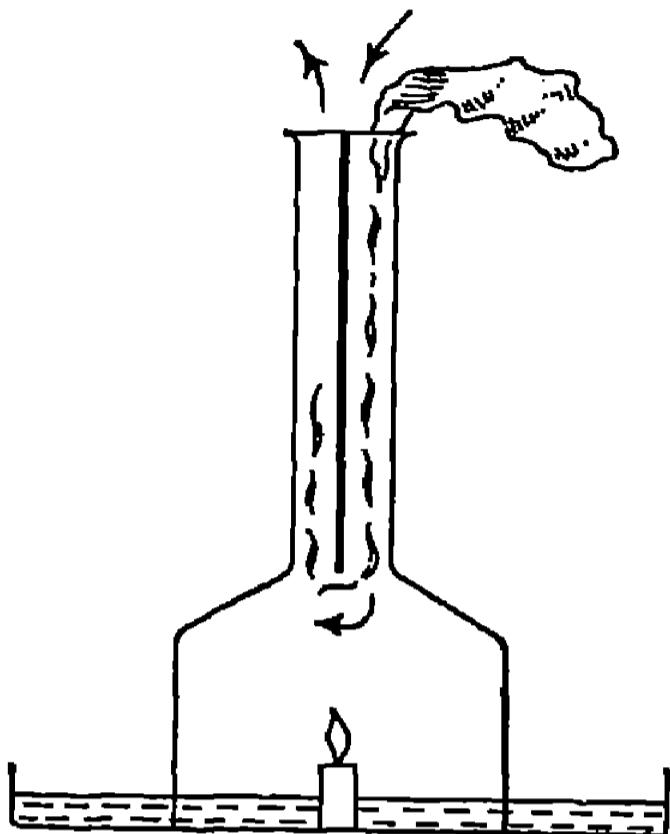
Fig. 1.—Convection in Gases

(a) *Land and Sea Breezes.*

It is observed at the coast that on an otherwise still, fine day there is a breeze which blows from sea to land in the morning and from land to sea in the evening. In the morning, the land having a lower specific heat than the sea is warmed more quickly by the sun's rays. Consequently, the air above the land is warmer than that above the sea. The former air therefore rises and the cool air from the sea flows in to take its place. In the evening the reverse process occurs. The land has acquired less heat than the sea since its specific heat is less; it therefore cools more quickly and the air above it becomes colder than that above the sea. The air above the sea now rises and the cool air above the land flows out to take its place.

(b) *Trade Winds.*

The air is hottest along the equator. It is therefore continually rising, and air flows in from either side, creating a northerly and southerly wind from the northern and southern hemispheres respectively. Owing to the rotation of the earth the winds are N.E. and S.E. and conditions are, of course, often complicated by local variations.

4. Convection in Liquids.

That convection occurs in liquids in readily shown by placing a few crystals of a coloured salt such as copper sulphate at the bottom of a flask containing water and heating locally at the centre of the

base of the flask. Streams of blue liquid arise from the bottom at the centre and travel upwards, returning down the sides, showing that the less dense, heated liquid is rising in the centre and the cold, denser liquid is flowing in from the sides to take its place.

Domestic hot-water systems are operated by convection as shown in fig. 2. Water heated by the fire rises to the top of the boiler B and proceeds along the upper exit pipe to the storage tank T. Cold fresh denser water enters the boiler by the lower entrance pipe. In this way a continuous circulation is set up. Hot-water " radiators ", both domestic and for automobiles, act in the same way. We may note,
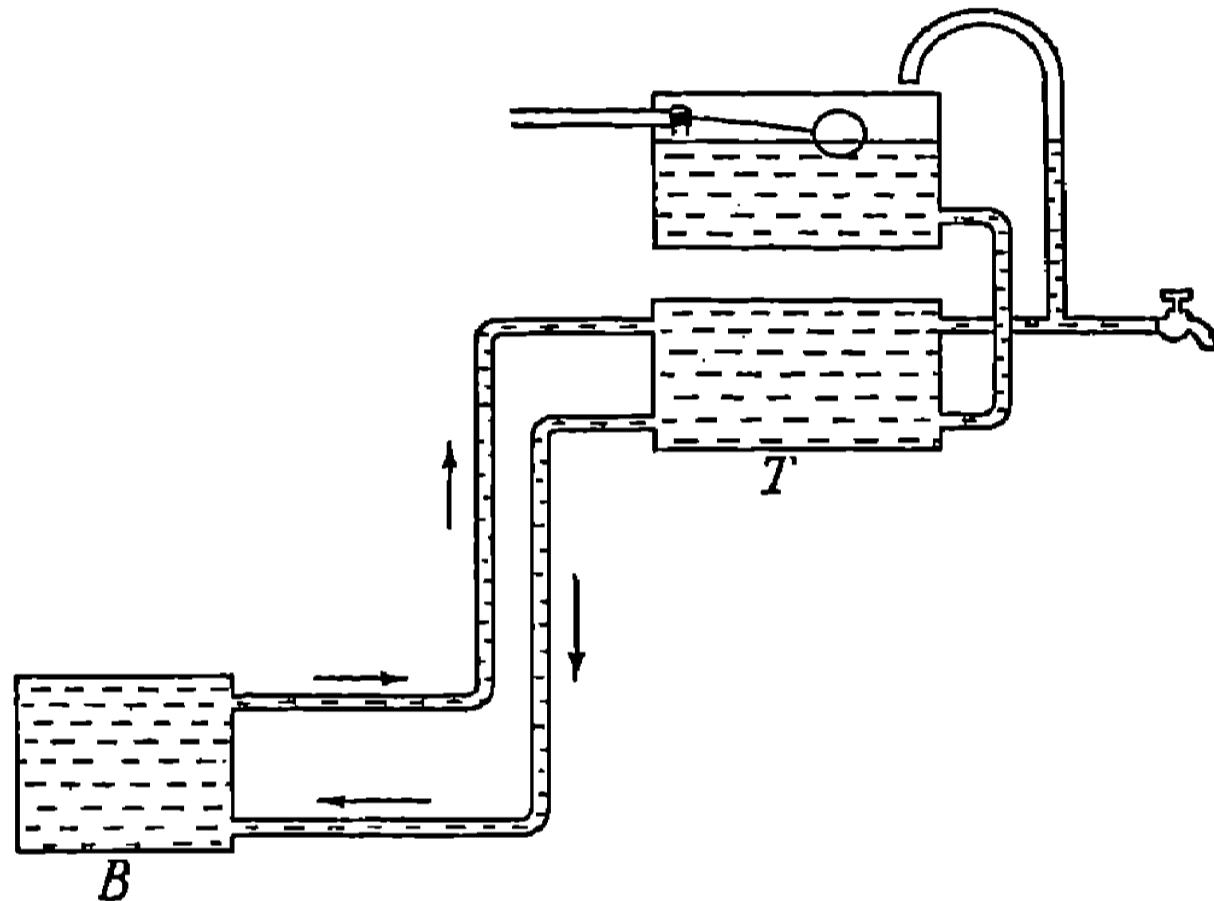
Fig. 2.—Domestic Hot-water System

however, that " convectors " would be a better name for " radiators ", since heat is given to the room mainly by convection of the air which takes place as the heated air rises continually from above the hot " radiator ".

5. Newton's Law of Cooling.

If in the experiment described on p. 29, on specific heat by the method of cooling, a cooling curve is plotted of temperature against time, its shape will be as ABC shown in fig. 3. Suppose now that tangents are drawn at various places on the curve to determine from the slopes of the tangents the rate of cooling, and another curve is plotted showing the variation of the rate of cooling with the excess temperature of the body above that of its surroundings. It will be found that provided the excess temperature is not too large the second curve is a straight line as shown in fig. 4. The *rate of cooling is proportional to the excess temperature*: this is **Newton's Law of Cooling**. The student should note that it applies to cooling by convection and

radiation, and therefore differs from Stefan's Law of Radiation (see Chap. XIV), which refers to radiation alone.

Since, according to Newton's law, the rate of cooling is proportional to the excess temperature, it follows that $f(\theta) = C\theta$ in equation
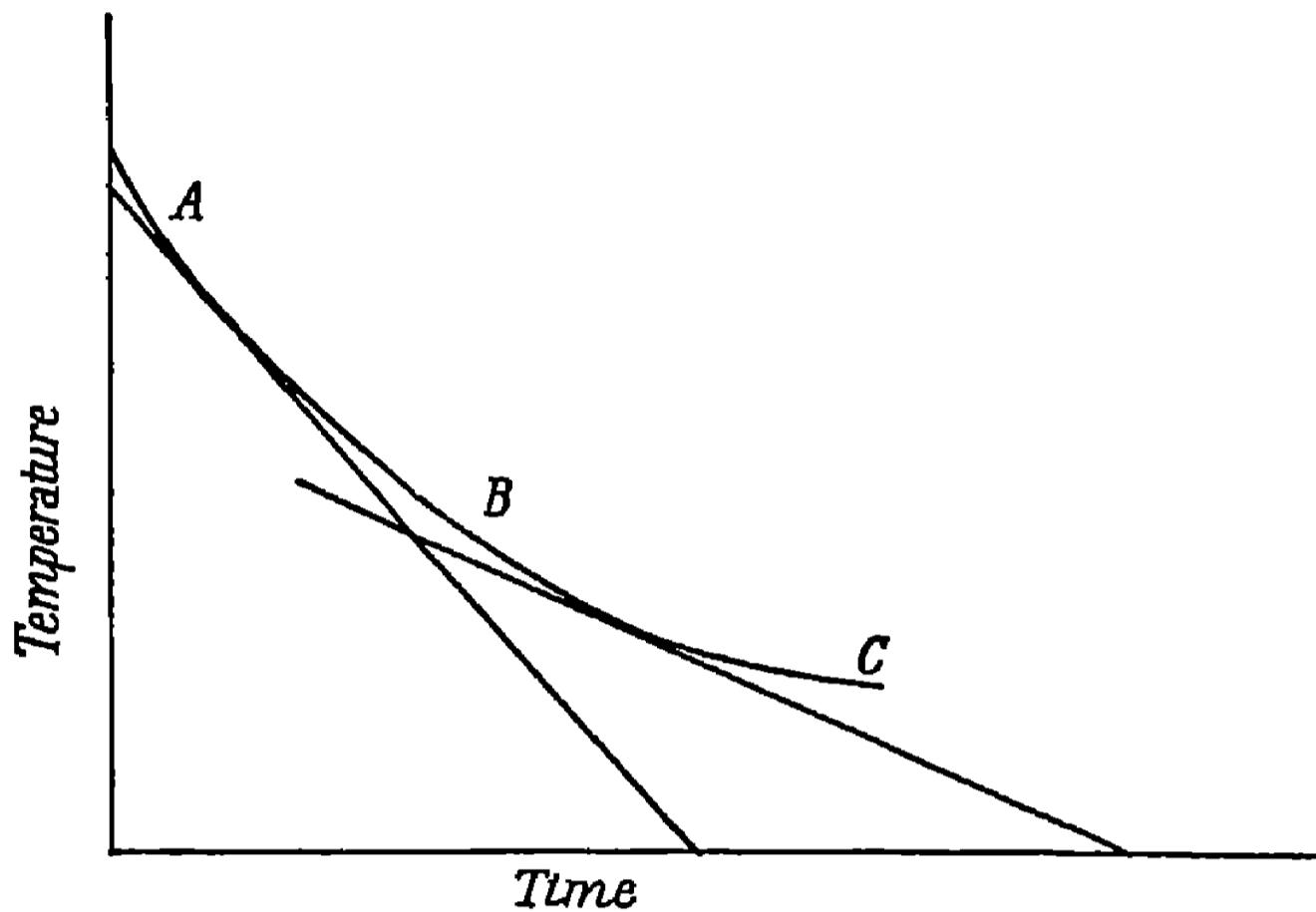
Fig. 3.—Cooling Curve

(3.8), where C is some constant depending on the nature of the surface of the calorimeter. Hence (3.8) becomes

$$dQ = CA\theta \ dt,$$

and since the area A is fixed for a given body, if we write $CA = D$, where D is a new constant,

$$dQ = D\theta \ dt. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.1)$$
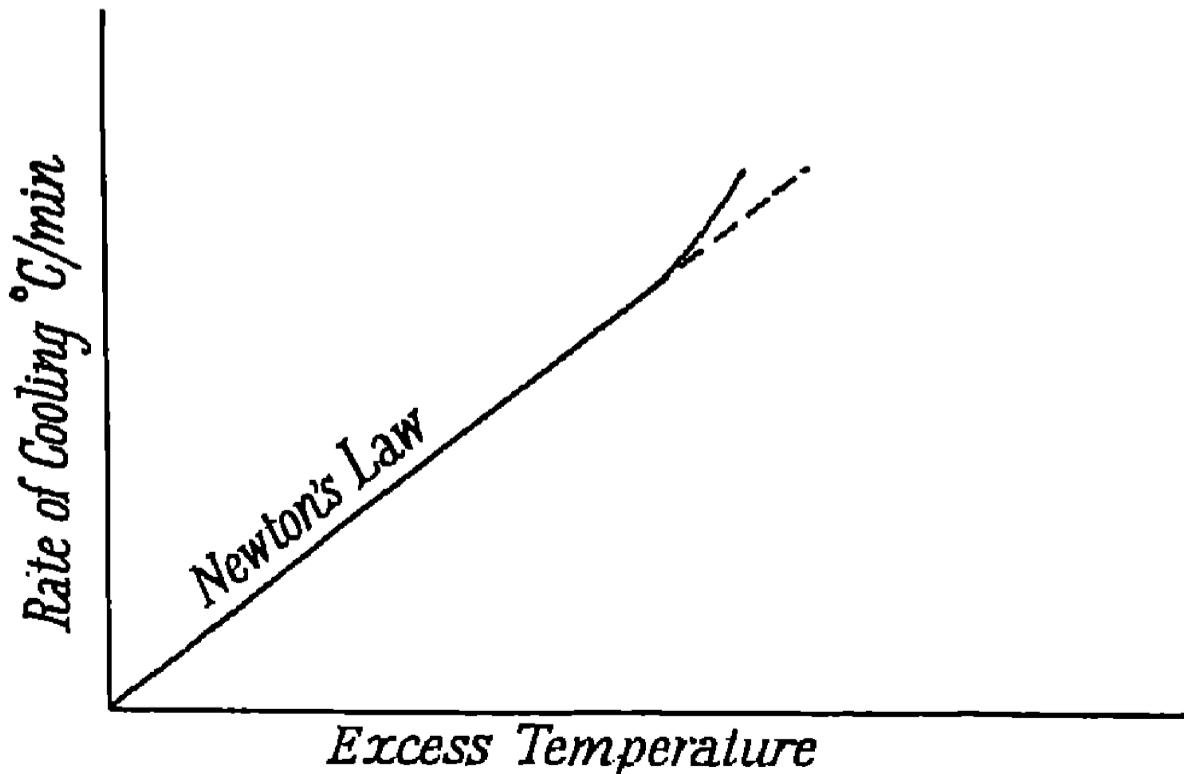
Fig. 4.—Newton's Law of Cooling

Combining equations (3.9) and (4.1),

$$dt = -\frac{ms\, d\theta}{D\theta}.$$

Integrating, we obtain

$$t = -\frac{ms}{D}\log_e\theta + B, \quad . \quad . \quad . \quad . \quad . \quad (4.2)$$

where B is a constant of integration.

To determine B we note that when $t = 0$, $\theta = \theta_1$, the initial temperature from which cooling starts. Hence

$$B = \frac{ms}{D}\log_e\theta_1,$$

and (4.2) becomes

$$t = -\frac{ms}{D}\log_e\frac{\theta}{\theta_1},$$

or

$$\theta = \theta_1\exp.\left(-\frac{D}{ms}t\right), \quad . \quad . \quad . \quad . \quad (4.3)$$

where exp. $(x) \equiv e^x$.

The cooling curve is therefore an **exponential curve** in the region over which Newton's law is obeyed. At higher temperatures the cooling is more rapid than Newton's law would indicate and no simple relation holds.

EXERCISES

1. Distinguish between natural and forced convection, and give examples to illustrate the part played by convection in atmospheric phenomena.

2. Describe how a cooling curve is constructed experimentally, and discuss the validity of Newton's Law of Cooling.

3. Distinguish between Newton's Law of Cooling and Stefan's Law of Radiation. Show that the former law follows algebraically from the latter for small temperature differences between a body and its surroundings. Is any theoretical significance to be attached to this agreement?

CHAPTER V

Thermal Conductivity

1. Introduction.

The fact that heat flows from one body to another when they are placed in contact, if a temperature difference exists between them, is attributed to **thermal conductivity**. On molecular theory, the temperature of a solid is proportional to the kinetic energy of the molecules. These molecules vibrate about fixed centres, and a higher temperature simply implies a larger amplitude of vibration. Thus if one end of a bar is heated, the molecules at this end are given a larger amplitude of vibration. The molecules impinge on the molecules in their immediate neighbourhood and cause them also to vibrate with larger amplitude. This process spreads along the whole bar, and is exhibited as the passage or conduction of heat down the bar.

2. Simple Experiments illustrating Thermal Conductivity.

If a piece of paper is wrapped round a roller consisting partly of wood and partly of iron, then on rotating the roller in a large flame a clear line of demarcation is observed, on one side of which the paper is badly charred while on the other it is scarcely singed. The charred side is found to cover the wooden portion and the uncharred the iron portion. The behaviour is attributed to the good thermal conductivity of iron and the poor thermal conductivity of wood. The iron conducts the heat away before the temperature can rise sufficiently to scorch the paper, whereas the wood is unable to conduct the heat away and therefore the paper burns.

That **liquids are poor conductors of heat** may be shown by sinking a small piece of ice with a lead weight to the bottom of a test-tube containing water. On applying a flame to the water at the top of the tube, the water may be boiled there for a considerable period before sufficient heat is conducted down through the water to melt the ice at the bottom.

The operation of the **Davy safety lamp** depends on the poor thermal conductivity of gases. The lamp consists of a metal gauze frame completely enclosing the naked flame. Should inflammable gas be present, the flame ignites the gas inside the gauze enclosure, but the heat from the flaming gas is conducted away along the metal gauze,

which is a good conductor. Consequently, as the **thermal conductivity of gas is poor,** its temperature does not rise sufficiently to ignite it outside the gauze enclosure. Of course, if the heat continues for long enough the gauze becomes red-hot and the outside gas is then ignited.

Many domestic applications of good and bad conductors will occur to the student, such as the introduction of badly conducting ivory rings into the handle of a metal teapot and the use of wooden knobs on kettle lids.

The best conductors are usually metals: in fact, the general rule that **good conductors of heat are good conductors of electricity** is well obeyed. However, there are no heat insulators of comparable efficiency with that of insulators of electricity.

3. Coefficient of Thermal Conductivity.

If we consider heat flowing normally across a flat slab of area A and small thickness dx, as shown in fig. 1, then it is found that the quantity of heat dq which flows normally across, in the direction in which x increases, in a small interval of time dt, is given by

$$dq = -k\,A\,\frac{d\theta}{dx}\,dt, \quad \ldots \ldots \quad (5.1)$$

where $d\theta$ is the small temperature difference existing between the two faces of the slab. The *minus* sign indicates that the flow of heat takes place in the direction in which θ decreases. In fig. 1, $d\theta$ is therefore *negative.* The quantity k depends on the nature of the substance and is termed the coefficient of thermal conductivity. From equation (5.1), if $A = dx = dt = 1$, and $d\theta = -1$, then $k = dq$, so k may also be defined as the *quantity of heat flowing per second across a cube of unit length of side, when the opposite faces are at unit difference of temperature.* However, the last definition implies that the **temperature gradient** $d\theta/dx$ is constant over a distance equal to the side of the cube, a state of affairs that may be difficult to realize.
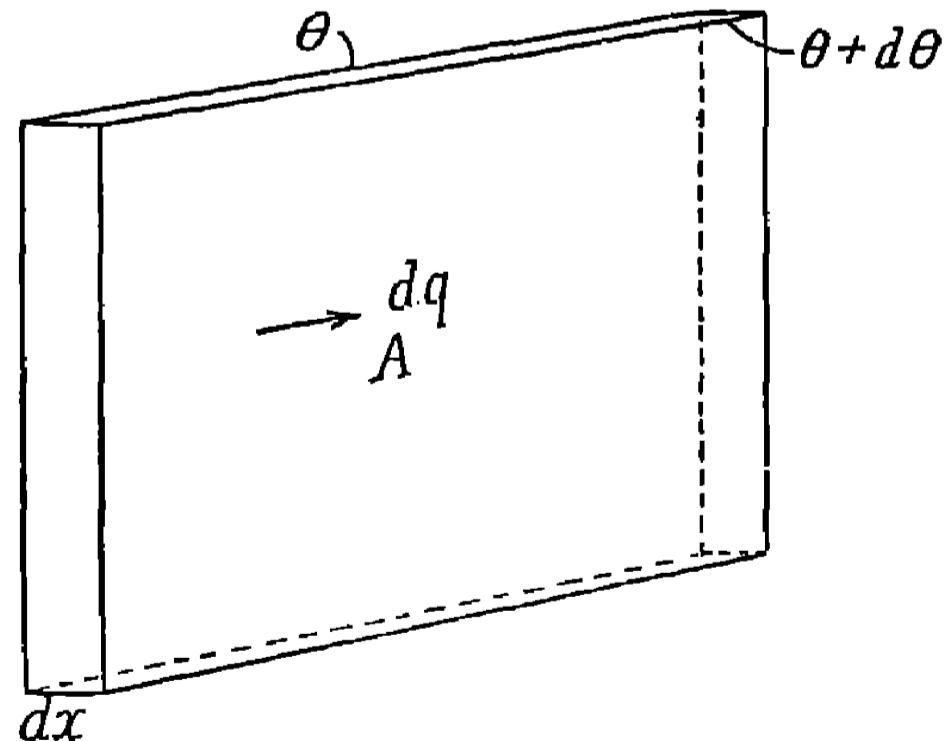

Fig. 1.—Flow of Heat across a Slab

When a rod is heated, the rate at which the far end becomes warm depends on the thermal capacity of the rod as well as on its thermal conductivity. If different rods of the same size are heated and we note the times taken for points at the same distance from the source to acquire the same temperature, these

times will be inversely proportional to the **thermal diffusivities** of the rods. The **coefficient of thermal diffusivity**, κ, is defined by the equation

$$\kappa = \frac{k}{\rho s}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.2)$$

where k is the thermal conductivity of the rod, ρ its density, and s its specific heat. The thermal diffusivity is therefore the thermal conductivity divided by the heat capacity per unit volume of the material. In all problems on thermal conductivity, unless the contrary is expressly stated, *steady conditions must be reached*: otherwise the thermal diffusivity and not the thermal conductivity may be involved.

All methods for both good and bad conductors depend on the application of (5.1) under certain conditions. The conditions are usually determined by the necessity to keep dq/dt a quantity of convenient magnitude: this is accomplished by making the area large and the thickness small for poor conductors, and conversely for good conductors. The former are therefore usually in the form of a slab and the latter in the form of a bar or rod.

* 3. Thermal Conductivity along Bars of Good Conductors.

Consider an element, length δx, of a bar as shown in fig. 2. If

θ = temperature of one face at plane x,

then $\left(\theta + \dfrac{d\theta}{dx}\,\delta x\right)$ = temperature of opposite face at plane $x + \delta x$;

and if $\quad q$ = heat entering first face in *unit time*,

and $\quad (q + \delta q)$ = heat leaving second face in unit time,

then by equation (5.1)

$$q = -kA\,\frac{d\theta}{dx},$$

and $\quad q + \delta q$ = new value of q when x becomes $x + \delta x$

$$= q + \frac{dq}{dx}\,\delta x$$

$$= -kA\left(\frac{d\theta}{dx} + \frac{d^2\theta}{dx^2}\,\delta x\right).$$

Hence the element would gain an amount of heat δq given by

$$\delta q = kA\,\frac{d^2\theta}{dx^2}\,\delta x. \quad . \quad . \quad . \quad . \quad . \quad (5.3)$$

Since the temperature of the rod is steady, this heat must be lost to the room in unit time. If we define the **emissivity** a of the rod *as the amount of heat lost per second per unit area of exposed surface per degree excess of temperature θ of the bar above its surroundings*, then
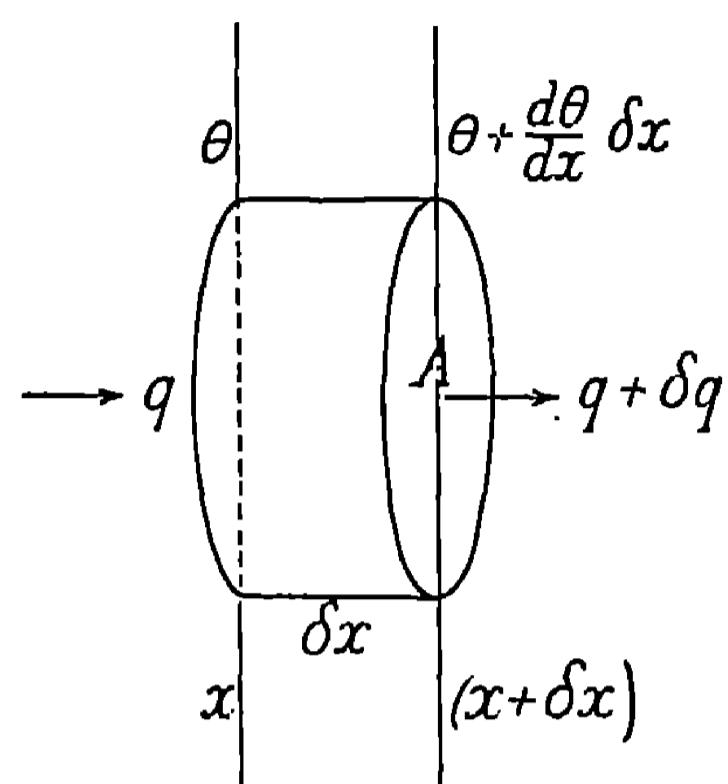
Fig. 2.—Flow of Heat across an Element of a Rod

$$\delta q = p \; \delta x \; \theta \; a, \quad . \quad . \quad (5.4)$$

where p = perimeter of the rod.
    Equating (5.3) and (5.4), we obtain

$$kA \; \frac{d^2\theta}{dx^2} = p \; \theta \; a. \quad . \quad (5.5)$$

Two cases usually present themselves experimentally. If the bar is lagged with a poor conductor, there is no loss of heat to the room from the sides of the rod, all the heat which enters one face of the bar being transmitted down the bar. Under these conditions

$$kA \; \frac{d^2\theta}{dx^2} = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.6)$$

Integrating equation (5.6) with respect to x,

$$kA \; \frac{d\theta}{dx} = \text{constant} = K, \quad . \quad . \quad . \quad . \quad (5.7)$$

which shows that the temperature gradient is constant. A graph of θ against x is therefore a straight line as shown in fig. 3, so that $d\theta/dx = (\theta_1 - \theta_2)/(x_1 - x_2)$.
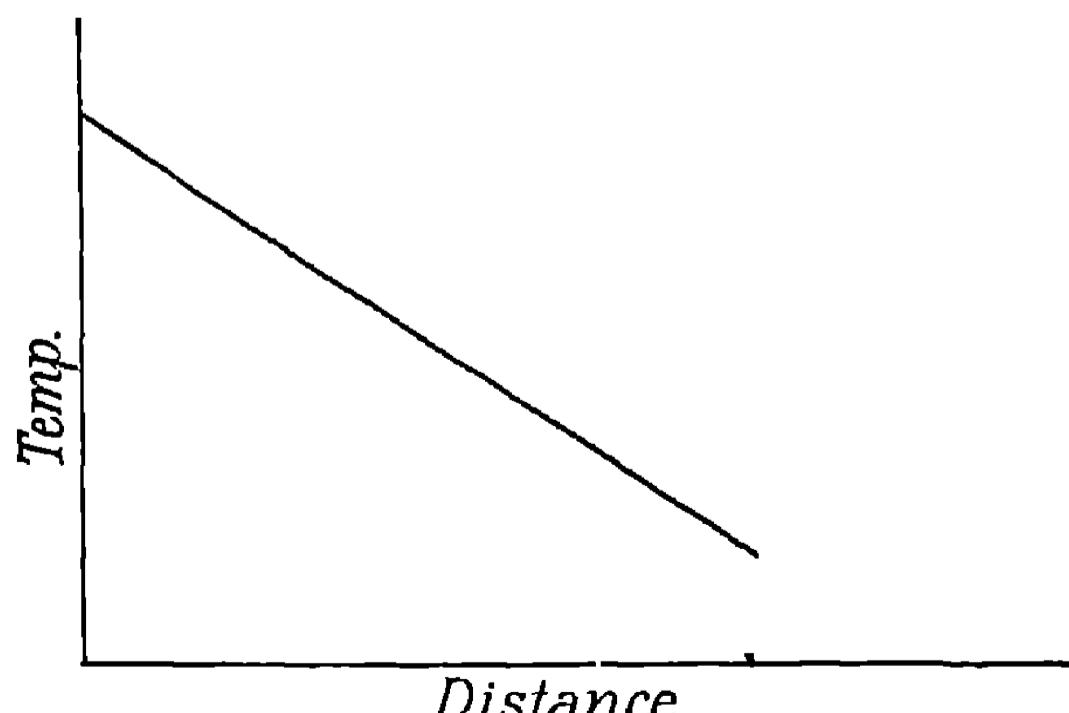
Fig. 3.—Uniform Flow of Heat along a Rod

From equation (5.1), $K = -dq/dt$; substituting this value in (5.7), we have

$$\frac{dq}{dt} = -kA \frac{(\theta_1 - \theta_2)}{(x_1 - x_2)}. \qquad . \quad . \quad . \quad . \quad . \quad (5.8)$$

Finally, integrating q with respect to t,

$$q = -kA \frac{(\theta_1 - \theta_2)}{(x_1 - x_2)} t. \qquad . \quad . \quad . \quad . \quad . \quad (5.9)$$
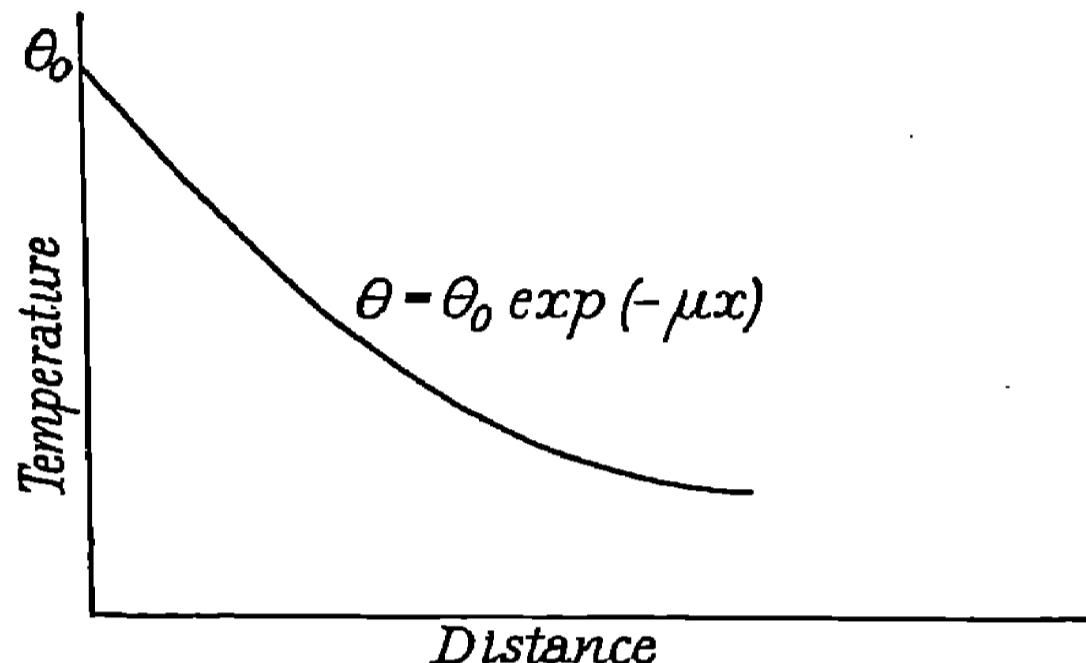
Fig. 4.—Temperature-Distance Curve for Exposed Bar

On the other hand, if the bar is freely exposed at the sides, equation (5.5) may be written

$$\frac{d^2\theta}{dx^2} = \frac{pa}{kA} \theta = \mu^2\theta, \qquad . \quad . \quad . \quad . \quad . \quad (5.10)$$

where $\qquad \mu^2 = pa/(kA).$

Integration of (5.10) gives

$$\theta = C \exp. (-\mu x) + D \exp. (+\mu x). \qquad . \quad . \quad (5.11)$$

To find C and D we note that for $x = \infty$ the temperature of the end of the bar will be that of the room, that is $\theta = 0$; hence $D = 0$. Finally, if θ_0 is the excess temperature above its surroundings at the high temperature end ($x = 0$) of the bar, substitution in (5.11) shows that $C = \theta_0$.

Hence

$$\theta = \theta_0 \exp. (-\mu x). \qquad . \quad . \quad . \quad . \quad (5.12)$$

The temperature-distance curve for an exposed bar is shown in fig. 4.

4. Experimental Methods for Good Conductors.

(a) Searle's Method.

In this method the material is in the form of a rod about 20 cm. long and 5 cm. diameter. Heat is supplied at one end by a jet of steam and the other end is cooled by contact with ice, as shown in fig. 5. Two thermometers are inserted symmetrically in the bar at a distance apart of about 10 cm.: if accurate results are required, thermocouples must be used so as to reduce the disturbance of the heat flow to a minimum. The whole bar is lagged with some bad conductor, such as cotton-wool, and when *steady conditions have been reached*, the rate
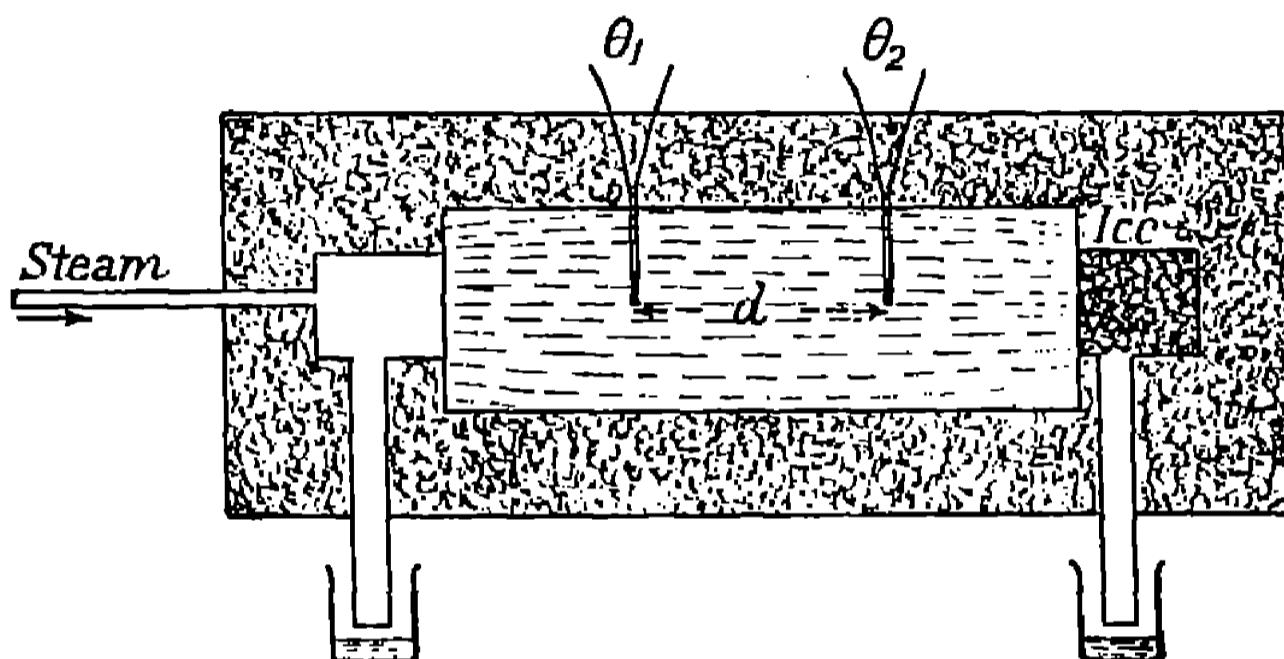
Fig. 5.—Searle's Method for Conductivity

of condensation of steam and the rate of melting of ice are observed, together with the temperatures θ_1 and θ_2 of the two thermometers. From fig. 5, the apparatus is seen to be so constructed that only the central portion of the bar is used. This is an example of the **guard-ring method** (we discuss this again in Part V). In this region the heat flow, as indicated by the broken lines, is normal to the restricted area A; consequently we may apply (5·9) or (5·1) directly and we have

$$q = m_1 L_1 = m_2 L_2 = kA \frac{(\theta_1 - \theta_2)}{d} t, \qquad . \quad . \quad (5.13)$$

where m_1 and m_2 are the masses of steam and ice collected in a time t, L_1 and L_2 are the latent heats of condensation of steam and melting ice respectively, d is the distance between the two thermometers, and A is the area of the central portion as shown in fig. 5.

(b) Forbes's Bar Method.

In this method, a bar some six feet long is taken and freely exposed to the air. One end of the bar is immersed in a constant temperature bath, while thermometers or, better, thermocouples are inserted

in the bar at regular intervals. When a steady state has been reached, the thermometers show the temperature distribution directly, and a curve is plotted of θ against x, which is the same as that shown in fig. 4. Tangents at any point of the curve give $d\theta/dx$ at that point. If we consider what becomes of the heat which crosses any cross-section of the bar at P, part of that heat travels down to the end of the bar, while the remainder is radiated from the sides. The quantity of heat q which flows across the bar at this point in one second is, by (5.1),

$$q = -kA\frac{d\theta}{dx}, \quad \ldots \ldots (5.14)$$

an equation in which q is unknown as well as k. To determine q, a short bar of the same material as the long bar is taken and heated to a temperature considerably above that of the point P in the first experiment, and a cooling curve is obtained. Now if another curve is constructed with rates of cooling ($-d\theta/dt$) as ordinates and corresponding values
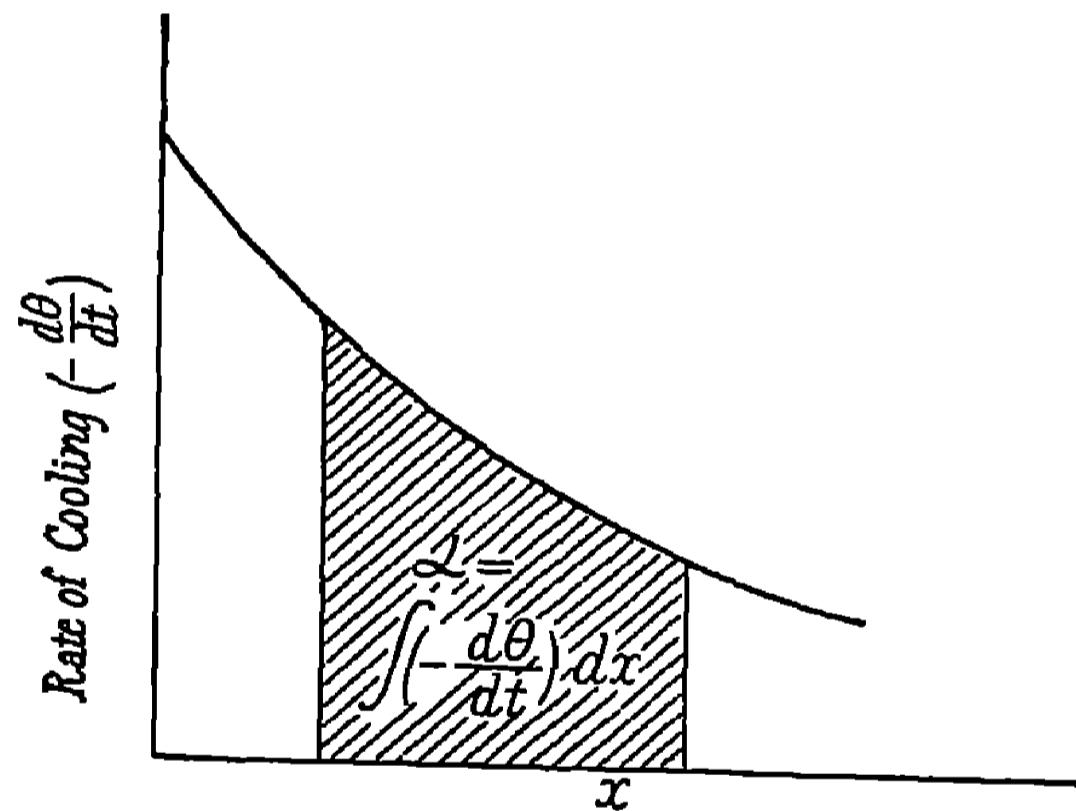
Fig. 6.—Forbes's Bar Method for Conductivity

of x as abscissæ as shown in fig. 6, the area α under the graph between any two values of x represents $\int\left(-\dfrac{d\theta}{dt}\right)dx$. But the amount of heat lost by an element of the rod of length dx in the neighbourhood of P in one second is

$$dq = \text{mass} \times \text{specific heat} \times \text{fall of temp.}$$

$$= \text{volume} \times \text{density} \times s \times \left(-\frac{d\theta}{dt}\right) \times 1$$

$$= A\,dx\,\rho s\left(-\frac{d\theta}{dt}\right).$$

Hence the total amount of heat lost beyond P between any two values of x is

$$q = A\rho s \int \left(-\frac{d\theta}{dt}\right) dx = A\rho s a. \quad . \quad . \quad . \quad (5.15)$$

But in the steady state (5.15) is equal to (5.14): hence

$$k = \frac{\rho s a}{(-d\theta/dx)}. \quad . \quad . \quad . \quad . \quad . \quad (5.16)$$

(c) *Ingenhausz's Experiment.*

For comparing thermal conductivities of metal rods an apparatus devised by Ingenhausz may be used. A number of metal rods of the
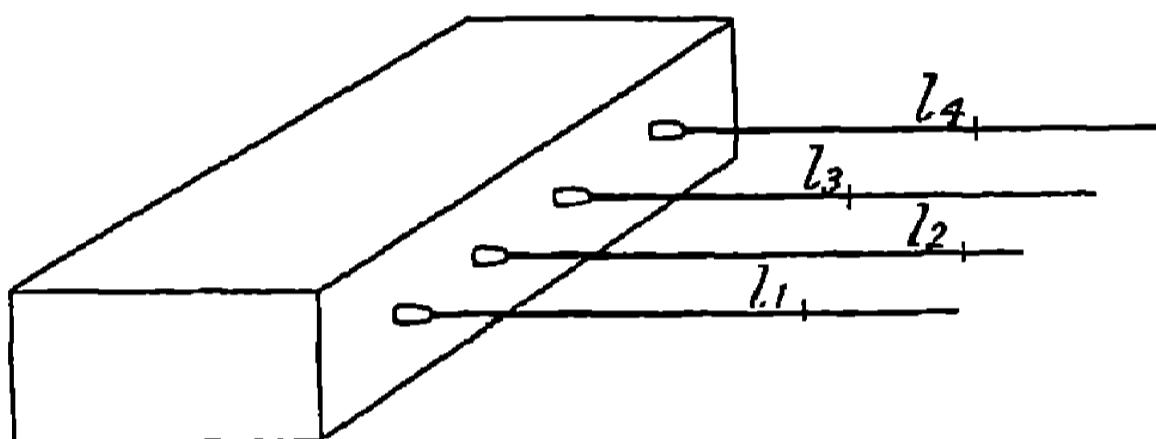
Fig. 7.—Ingenhausz's Experiment

same length and diameter are coated with the same material, say lamp-black, and then arranged with one end in a common temperature bath as shown in fig. 7. The rods are also coated with wax, and when steady conditions are reached it is found that the wax has melted for different lengths l_1 and l_2 on rods of different materials. If k_1 and k_2 are the thermal conductivities of the two rods,

$$\frac{k_1}{k_2} = \frac{l_1^2}{l_2^2}. \quad . \quad . \quad . \quad . \quad . \quad (5.17)$$

To show this, if we apply equation (5.12) to each rod we have

$$\theta_{\text{wax}} = \theta_0 \exp. (-\mu_1 l_1),$$
$$\theta_{\text{wax}} = \theta_0 \exp. (-\mu_2 l_2),$$

where θ_{wax} is the melting-point of the wax.

Hence

$$\frac{l_1}{l_2} = \frac{\mu_2}{\mu_1},$$

and from (5.10), since p, a and A are the same for both rods, $k_1/k_2 = l_1^2/l_2^2$.

5. Thermal Conductivity of Bad Conductors.

(a) Tube Method.

If the conductor (for example, rubber) can be made in the form of a tube, a convenient arrangement is to coil the tube inside a calorimeter containing water and to pass steam through the tube. The heat passing through the tube is measured by the rise in temperature of the calorimeter. For this case, equation (5.1) gives, for the heat crossing unit length of a section of radius r,

$$dq = -k(2\pi r)\frac{d\theta}{dr}\,dt,$$

or

$$\frac{1}{r}\frac{dr}{d\theta}\frac{dq}{dt} = -2\pi k.$$

Since dq/dt at a particular moment is the same at all sections, integration gives

$$\left(\log_e \frac{r_2}{r_1}\right)\frac{dq}{dt} = 2\pi k(100 - \theta'),$$

where θ' is the temperature of the tube next the water, i.e., approximately, of the water itself; we may assume for simplicity that θ' increases uniformly with the time. A further integration with respect to t then gives for k the equation

$$\left(\log_e \frac{r_2}{r_1}\right)\frac{q}{t} = 2\pi k\left(100 - \frac{\theta_1 + \theta_2}{2}\right), \quad . \quad . \quad . \quad (5.18)$$

where θ_1, θ_2 are the initial and final temperatures of the water. The value of $q = W(\theta_2 - \theta_1)$, where W is the water equivalent of the calorimeter and contents, and $(\theta_2 - \theta_1)$ is the rise in temperature during the time t. The method is not very satisfactory since r_2 is nearly equal to r_1; also the conditions are not steady, the temperature rising from θ_1 to θ_2 on one side of the tube during the experiment.

(b) Lees's or the Slab Method.

A good form of this apparatus is shown in fig. 8. It consists of a flat slab of the material X whose thermal conductivity is required, enclosed between two flat metal sheets. Next in the "sandwich" is a flat spiral heating coil, and finally, covering this, another flat metal disk. The whole is covered with shellac and suspended in a uniform temperature enclosure by the wires which serve to supply current to the heating coil. Energy is supplied to the coil and steady excess temperatures θ_1, θ_2 and θ_3 are registered by thermocouples in contact with the appropriate surfaces as shown in fig. 8. Then if we define the

emissivity a of the shellaced surface as on p. 43, when equilibrium is established

$$H = \frac{EI}{J} = aS_1\theta_1 + aS\frac{(\theta_1 + \theta_2)}{2} + aS_2\theta_2 + aS_3\theta_3, \quad (5.19)$$

where H is the rate of heat supply, E and I are the average potential difference across and current through the heating coil, J is Joule's mechanical equivalent of heat, and S, S_1, S_2 and S_3 are the exposed areas of the specimen and disks respectively. Equation (5.19) determines the emissivity a.

If attention is now concentrated on the heat which passes *normally* through the specimen X per second, this heat q is the average of the heat entering and the heat leaving X. In the steady state the heat entering is the total amount of heat which leaves the surface of X and the lower disk, while the heat leaving is that which leaves the lower disk: hence

Fig. 8.—Lees's Method for Conductivity

$$q = \frac{kA}{d}(\theta_1 - \theta_2) = \frac{1}{2}\left[\left\{aS\frac{(\theta_1 + \theta_2)}{2} + aS_2\theta_2\right\} + aS_2\theta_2\right]$$

$$= aS\frac{\theta_1 + \theta_2}{4} + aS_2\theta_2, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (5.20)$$

where k = thermal conductivity of the specimen,
            A = area of cross-section of specimen,
            d = thickness of specimen,

and $\dfrac{(\theta_1 + \theta_2)}{2}$ = mean excess temperature of specimen.

Since a has been determined from (5.19) all the quantities in (5.20) are known except k.

The method may be applied to find the thermal conductivity of liquids and gases. The slab X consists of a hollow flat cylindrical box of glass. This is filled with the liquid or gas under test and the heating coil is arranged to be vertically above X to avoid convection currents. The box X is then evacuated and the experiment repeated to provide a correction for the heat conducted down the sides of the container. The thermal conductivity of gases is of particular interest on the kinetic theory as shown in Chap. XI. At *low* pressures, the thermal conductivity varies directly as the pressure, and this fact forms the basis of thermal conductivity pressure gauges.

EXERCISES

1. What factors govern the design of apparatus for measuring the thermal conductivity of solids?

Describe an *accurate* method for measuring the thermal conductivity of a good conductor.

2. Distinguish between thermal conductivity and thermal diffusivity.

Describe Ingenhausz's experiment for comparing the thermal conductivities of substances, and indicate how the required formula is derived.

3. Show theoretically that the distribution of temperature along a bar heated at one end and subject to steady conditions is (*a*) a straight line for a lagged bar, (*b*) an exponential curve for a bar which is freely exposed.

4. Describe the Forbes's bar method of measuring the thermal conductivity of a metal, giving the theory of the method.

5. If the air above a lake is at a steady temperature of $-1°$ C., determine how long it will be before it is safe to skate, given that the water is initially at $0°$ C. and that safe skating requires a thickness of 10 cm. of ice. The density of ice is 0.92 gm./c.c., its thermal conductivity is 5×10^{-3} cal. cm.$^{-1}$ °C.$^{-1}$ sec.$^{-1}$, and the latent heat of solidification is 80 cals./gm. [204·4 hr.]

6. How may the coefficient of thermal conduction of a liquid be measured?

What is the explanation of thermal conduction on the kinetic theory of matter?

7. Describe the tube method for finding the thermal conductivity of a poor conductor.

Two flat metal plates are placed with their surfaces in contact, and these surfaces are maintained at temperatures of $100°$ C. and $0°$ C. respectively. If the thicknesses of the plates are 2 cm. and 1 cm. and their thermal conductivities are 0.1 and 0.2 C.G.S. units, find the temperature of the common surface. [20° C.]

CHAPTER VI

Heat, Energy, and Joule's Law

1. Forms of Energy.

We have already discussed briefly the nature of energy in Part I, Chap. III, section 5. We may note here that energy can occur in at least ten different forms, namely:

(1) *Kinetic energy.*
(2) *Potential energy.*
(3) *Heat energy.*
(4) *Strain energy.*
(5) *Sound energy*—compounded of (1), (2), and (4).
(6) *Light and radiant energy.*
(7) *Electrical energy*
(8) *Magnetic energy*
(9) *Chemical energy* $\Big\}$ not directly detected by the senses.
(10) *Sub-atomic energy*

Whenever energy disappears from one of these forms it reappears in another form. In this chapter we give the evidence on which this qualitative fact is transformed into a strict quantitative relation for the transformations, *mechanical energy → heat energy*, and *electrical energy → heat energy*. That is, we proceed to show that it is found experimentally that whenever a given quantity of mechanical or electrical energy disappears, a definite quantity of heat energy makes its appearance. This relation is sometimes termed the **First Law of Thermodynamics**, and is expressed mathematically as

$$W = JH, \qquad \ldots \ldots \ldots \quad (6.1)$$

where W is the mechanical energy which disappears and H is the corresponding quantity of heat energy formed. The ratio J is termed **Joule's equivalent of heat** and has a value of 4.18×10^7 ergs per calorie.

2. Joule's Determination of J.

One form of the apparatus used by Joule about 1848 is shown in fig. 1. Two masses M_1, M_1 were attached to a cord passing round a vertical drum, rotation of the drum taking place when the weights

were allowed to descend vertically. The axle of the drum was attached to a paddle system which stirred water contained in a cylindrical calorimeter. Radial stops in the calorimeter were staggered with the paddles, so that churning of the water took place and the liquid did not rotate as a whole. The suspended masses were between 10 and 30 lb. and the mass of water stirred was about 8 lb. The calorimeter was of copper and there were 8 paddles made of brass. The height through which the masses fell was 5 ft., and they were allowed to fall 20 times in succession. The rise in temperature of the water was then measured
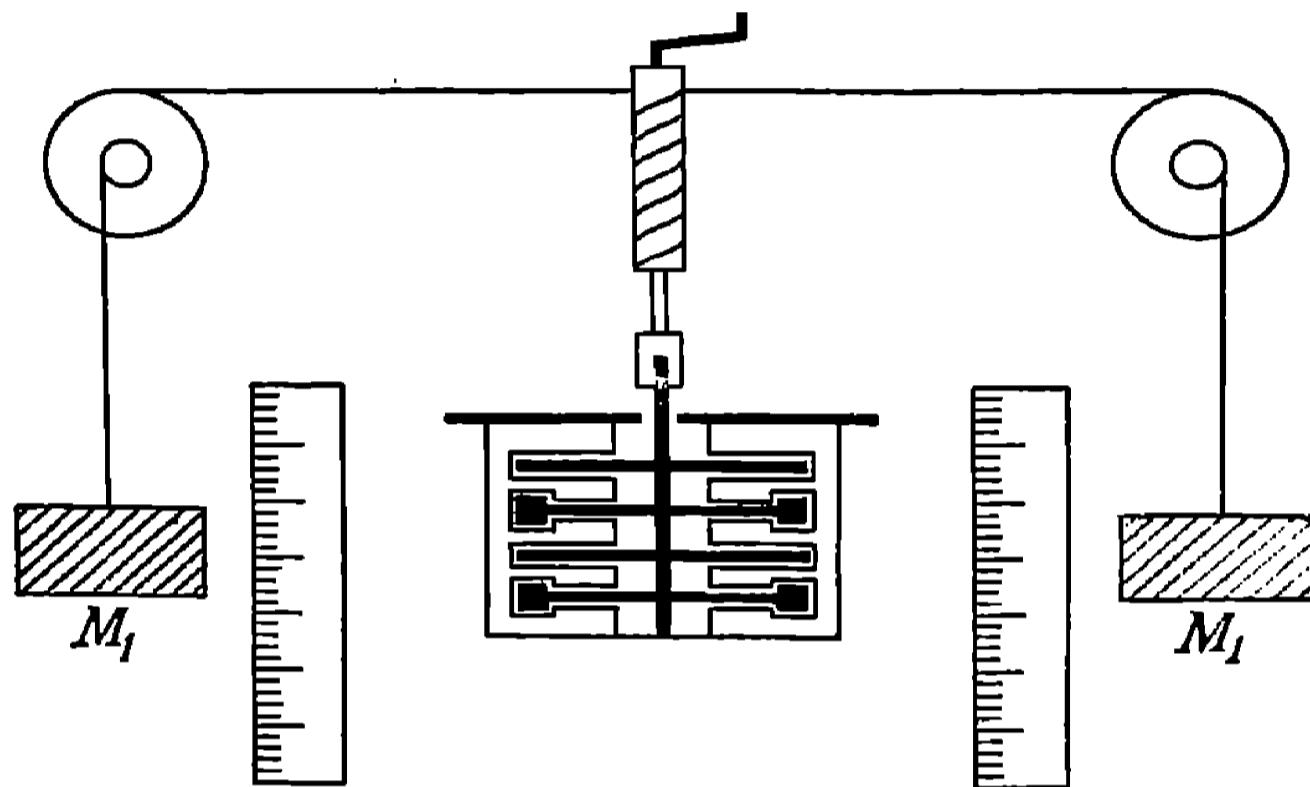
Fig. 1.—Joule's Apparatus

and found to be about 0·5° F. Since the mechanical energy destroyed was $W = nmgh$, where

n = number of times of fall,
m = mass of both weights,
g = acceleration due to gravity,
h = distance fallen,
and $H = C\theta$, where
C = water equivalent of calorimeter and contents,
θ = rise of temperature,

it follows from equation (6.1) that

$$J = \frac{W}{H} = \frac{nmgh}{C\theta}. \qquad \qquad (6.2)$$

Several corrections were necessary to obtain an accurate result. These were:

(1) The potential energy of the weights was converted partly into kinetic energy as well as into heat. The terminal velocity of fall of the weights was determined to be about 1 in. per second. The corre-

sponding kinetic energy had to be subtracted from W to give correct results in equation (6.2).

(ii) To allow for the energy lost in overcoming the friction of the pulleys, a small additional weight had to be attached to the masses to give steady motion. This method of allowing for friction is the same as that used on p. 56, Part I, in determining g with Atwood's machine.

(iii) All the usual corrections for loss of heat in calorimetry, as discussed in Chap. III, p. 28, had to be taken into account. The small rise in temperature tended to make these corrections small, but this advantage was offset to some extent by the comparatively long time of the experiment.

To show that J was a fundamental quantity, independent of the method used, Joule carried out many other experiments. Thus he used iron paddles moving in mercury and, in another experiment, two iron rings rubbing together under mercury. He also used electrical methods, his first method being to find the heat generated in a wire carrying the electric current from a dynamo which was consuming a measured quantity of mechanical energy to drive it. Electrical methods now give the most accurate value of J, but at the time Joule worked the electrical units of current, resistance and potential difference were only approximately defined.

Finally, Joule obtained a value for J from the heat developed in a gas when mechanical work is done in compressing the gas suddenly. The work done on adiabatic compression could be calculated as shown in Chap. XII, section 4, but the heat could not be measured accurately owing to the relatively large heat capacity of container and thermometers, compared with that of the gas itself.

3. Later Mechanical Experiments.

In 1879, Rowland carried out some accurate measurements of J, using a steam-engine to drive the paddle. In this way, with a rate of working of 2200 kg. metres/min. a rise in temperature of 25° C. was obtained in 40 min. Mercury thermometers were used, but these were calibrated against a standard hydrogen gas thermometer. Rowland's experiments were sufficiently accurate to show the existence of a variation in the specific heat of water with temperature.

Some years later, Callendar used a somewhat similar method, an electric motor being used to drive a rotating cylindrical calorimeter mounted on a horizontal axis, the heat being produced by the friction of a silk band pressing against the outer surface of the calorimeter. The mechanical energy used was determined by using the band as a brake tester as described in Part I, pp. 42-43.

4. Electrical Methods.

We have already described the electrical methods briefly in Chap. III, section 6. Joule's electrical method was carried out accurately by *Griffiths* in 1894 and by *Jaeger* and *Steinwehr* in 1921. In Griffith's experiment, the potential difference E and the resistance of the wire R were determined, and a vacuum jacket was used to reduce heat losses. A platinum wire 33 cm. long and of about 9 ohms resistance was used in a cylindrical calorimeter about 8 cm. high and 8 cm. diameter. Electrical energy was supplied by 3 and 6 Clark cells respectively; if E is the E.M.F. of one cell, equation (3.14) becomes

$$\frac{E^2}{R}\frac{1}{J}(4t_2 - t_1) = (m - m')s\theta, \quad \ldots \quad (6.3)$$

where s was unity for water, and t_2 was the time of the second experiment and was approximately equal to t_1 so that the heat losses were approximately the same in the two experiments. The quantity $(m - m')$ was about 120 gm.; a disadvantage of the method lies in the variation of R with temperature.

Callendar and *Barnes* determined J by the continuous flow method which has also been described in Chap. III, section 6. *Thermocouples* were used to measure the inlet and outlet temperatures and a very accurate value of J was obtained.

Recently Hercus and Laby have used a combination of Joule's first method and the continuous flow method. A copper tube stator conveying water is used as the flow tube, and a magnetic field rotates around this. Electrical energy is produced by electromagnetic induction and is converted into heat, the mechanical energy absorbed being determined with a brake tester.

5. J by the Reverse Process.

Equation (6.1) is strictly reversible, and it is possible to obtain a value for J by measuring the quantity of mechanical energy resulting from the transformation, heat energy → mechanical energy. The accuracy of the measurements does not approach that of the preceding methods, so we shall simply describe very briefly one experiment carried out by Hirn about 1860. A measured quantity of heat Q was taken from the boiler of a steam-engine and it was found that a smaller quantity q was given up to the condenser (see Chap. XIII). If W was the mechanical work performed by the steam-engine during this process, it was found that J satisfied the relation

$$W = J(Q - q - R), \quad \ldots \quad (6.4)$$

where *R* was a correction applied for the heat losses suffered by the engine. As the efficiency of a steam-engine is only a few per cent, the correction *R* was very large.

EXERCISES

1. Write a short essay on the Conservation of Energy, with special reference to the First Law of Thermodynamics.

2. Describe Joule's apparatus for measuring the mechanical equivalent of heat, pointing out the corrections necessary to obtain an accurate value.

3. Describe an electrical method for finding Joule's equivalent of heat.

Find the percentage heat lost if 100 gm. of liquid of specific heat 0·3, contained in a copper calorimeter of mass 200 gm. and specific heat 0·094, is raised in temperature by 10° C. in 150 sec. when an immersed coil of wire carries a current of 4 amp. under a potential difference of 4 volts. [15 per cent.]

4. Taking the specific heat of lead as 0·03, find the rise in temperature of a lead bullet if it remains embedded in a fixed, badly-conducting block. The initial velocity of the bullet was 100 cm./sec., and 95 per cent of its kinetic energy was converted into heat. Joule's equivalent of heat is $4·2 \times 10^7$ ergs/cal. [$3·8 \times 10^{-3}$ ° C.]

CHAPTER VII

Thermal Properties of Gases

1. Deviations from Boyle's Law.

As we have seen in Part I, Chap. X, section 5, at constant temperature, the pressure of a given mass of gas is inversely proportional to its volume. This statement constitutes Boyle's law, and within the limits of the experiment described on p. 107, Part I, it would be found to be true for what are sometimes termed the "permanent"
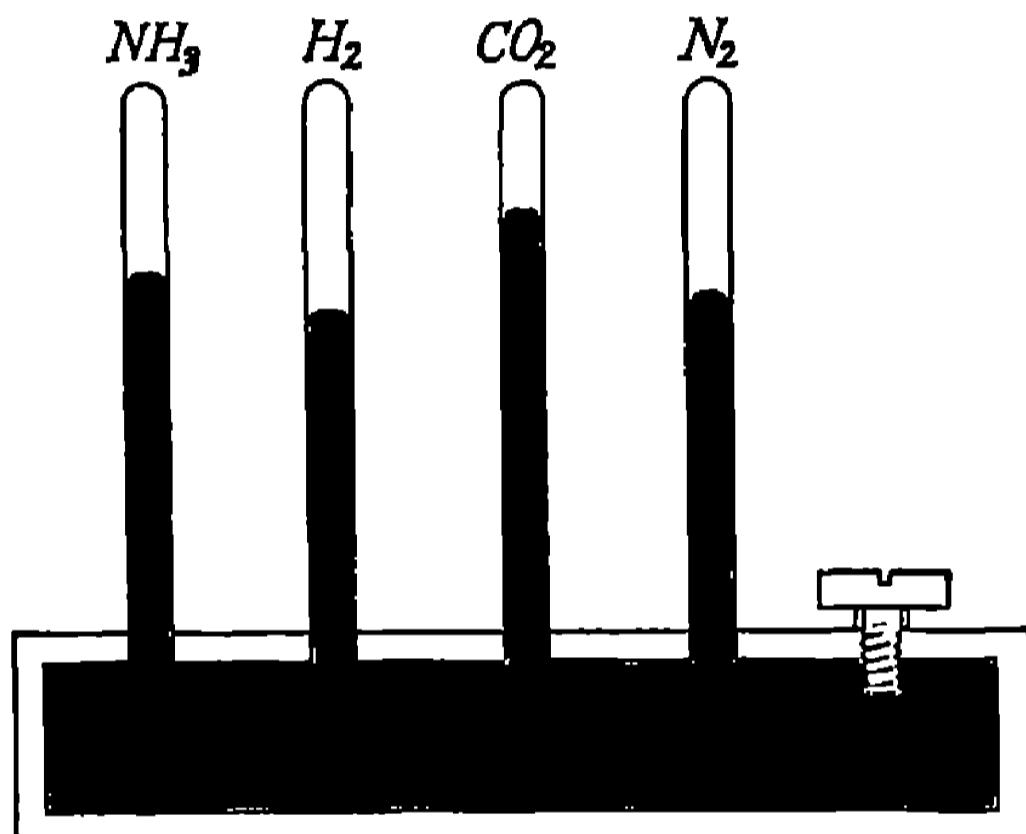
Fig. 1.—Deviation of Gases from Boyle's Law

gases, of which examples are hydrogen, oxygen, nitrogen, and the rare gases. Actually, Despretz showed as early as 1827 that gases such as carbon dioxide and ammonia were more compressible than if they had strictly obeyed Boyle's law. The apparatus, as shown in fig. 1, consisted of a number of barometer tubes cemented into a closed cistern containing mercury. Initially, the volume of different gases contained in the tubes was the same, but on raising the pressure by screwing a plug into the cistern the mercury rose much faster in the tubes containing the carbon dioxide and ammonia than in the tubes containing the "permanent" gases.

The simple Boyle's law apparatus hitherto described is clearly not capable of great accuracy at high pressures, since the volume of gas becomes very small indeed. Accordingly, in 1847 Regnault introduced the apparatus shown in fig. 2. The gas is contained in a vertical glass

tube fitted at the top with a tap which communicates with a compression pump. A mark at the centre of the tube indicates the half-volume position; pressure is applied by a mercury column which is attached to a force-pump. Let us suppose the gas is initially at atmospheric pressure p, when it just fills the tube. The tap T is then closed and the pressure increased until the volume is halved. If Boyle's law is exactly obeyed the new pressure p_2 will be exactly equal to twice p_1, that is, the ratio $2p_1/p_2$ should equal unity. In the first pair of readings with permanent gases this is approximately true. The experiment is continued by pumping more gas in through T so as to depress the mercury back to its original position; then T is again closed. The gas will now be at some new pressure p_3, and we may again halve the volume by raising the pressure to p_4. If Boyle's law were still true $2p_3/p_4$ will also equal unity, but that is not found experimentally. In fig. 3 is shown a graph exhibiting the variation of pv with p. As the pressure is increased, most gases at room temperature show a value of

Fig. 2.—Regnault's Apparatus for testing Boyle's Law

pv which decreases as the pressure increases. A minimum value is eventually reached, after which pv increases indefinitely with rise of pressure. On the other hand, hydrogen and helium, *at room temperature*, show a steady increase in the value of pv from very low pressures.
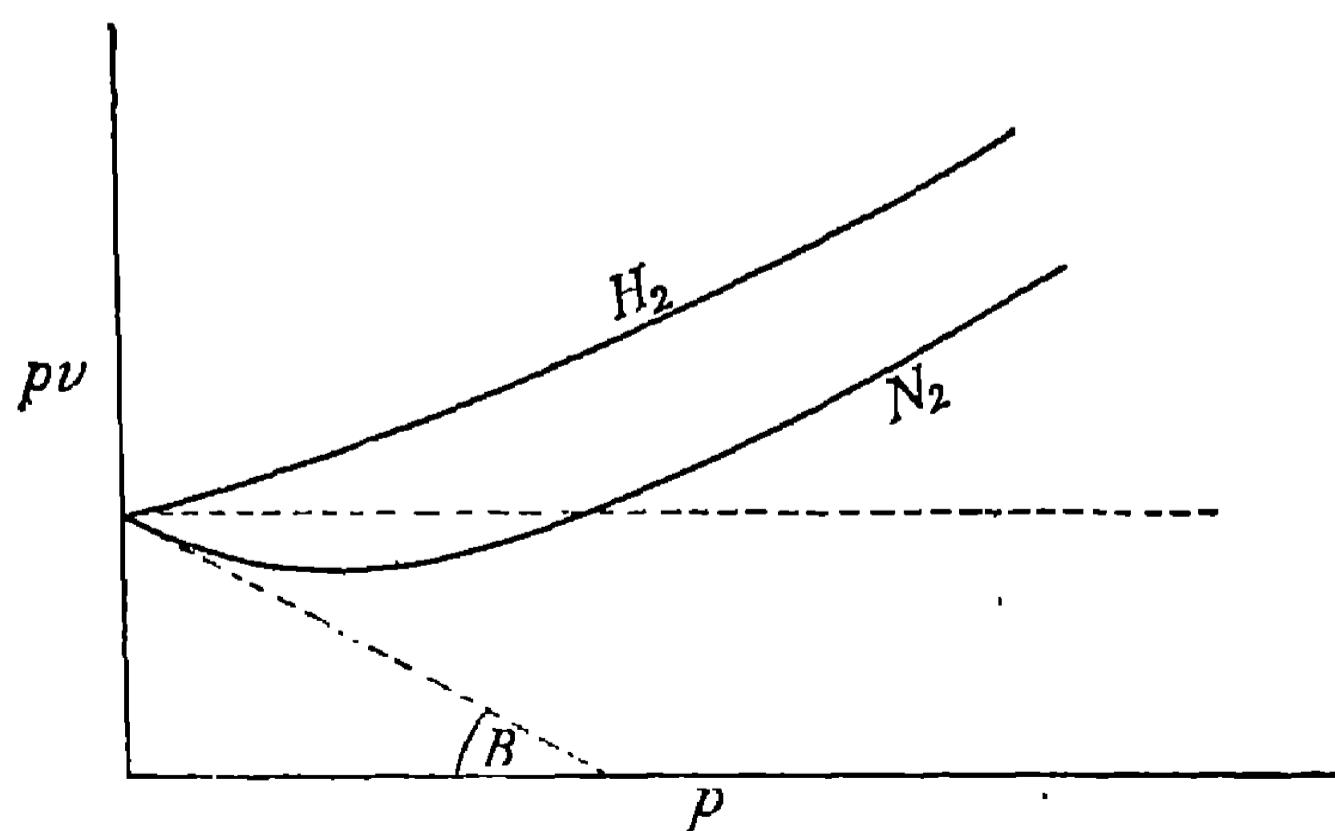
Fig. 3.—Graphs of pv against p for Hydrogen and Nitrogen

For very accurate work Boyle's law must be replaced by some
·more general equations.   Of those which have been proposed we note
first an empirical relation suggested by Holborn and Otto, namely

$$pv = A + Bp + Cp^2 +, \&c., \quad . \quad . \quad . \quad . \quad (7.1)$$

where A, B, &c., are constants at constant temperature and are termed
virial coefficients.   Such an equation has no theoretical basis and is
useful simply as a method of expressing the experimental results.   The
virial coefficients are such that $A \gg B \gg C$ and so on.   At low pres-
sures, therefore, Boyle's law is approximately true, whereas as the
pressure is increased more and more terms become necessary in equa-
tion (7.1).   We may note that $d(pv)/dp$ is the slope of the tangent to
the curve in fig. 3.   Differentiating (7.1) and putting $p = 0$, we find
that the slope of the tangent at the commencement of the curve is
the virial coefficient B.   Since this slope is negative for most gases at
room temperature, B is usually negative.   Graphs are available showing
the variation of B with temperature; the temperature for which $B = 0$
·is termed the *Boyle temperature*, for at this temperature Boyle's law is
obeyed for a considerable range of pressure.

As we shall see in Chap. XI, the deviations of gases from Boyle's
law receive a ready explanation on the kinetic theory.   Again, in
Chap. X, we discuss Van der Waals' equation as a more satisfactory
description of real gases than the perfect gas equation.

2. Thermal Expansion of Gases.

When gases are heated they show much more expansion than
solids and liquids.   In general, not only the volume increases but also
the pressure.   If the gas is heated in a closed vessel the volume per-
force remains constant and the pressure increase is then a maximum.
Conversely, if the gas is allowed to expand by a suitable amount
then the pressure may be kept constant.   **Charles's constant pressure
law** states that *at constant pressure, for a rise in temperature of 1° C.,
all gases expand by a constant amount, equal to about 1/273 of their
volume at 0° C.*   This behaviour of gases is in striking contrast with
that of solids and liquids, both in the magnitude of the expansion
coefficient and in the fact that the expansion coefficient of all gases
is the same.   Actually, as with Boyle's law, Charles's pressure law
is obeyed best by the permanent gases.   Expressed mathematically,
the law states that

$$v = v_0(1 + \gamma t), \quad . \quad . \quad . \quad . \quad . \quad (7.2)$$

where $v =$ volume at temperature $t°$ C.,
      $v_0 =$ volume at 0° C.,
      $\gamma = 1/273$ approximately.

Equation (7·2) is formally similar to equation (2·7), but the difference lies in the fact that in the latter v_0 refers to the volume at any lower temperature, whereas, for gases, $\gamma = 1/273$ only if v_0 is the volume at 0° C. Equation (7·2) shows the surprising result that if $t = -273°$ C., $v = 0$, or the gas would contract to zero volume if it continued to obey Charles's pressure law. Actually, the gas liquefies and solidifies before this temperature is reached, but it is convenient to adopt $-273°$ C. as the natural zero for a **gas scale of temperature** for an ideal gas. If instead of keeping the pressure constant and allowing the volume to change the volume is kept constant, it is found that the pressure changes by a law exactly similar to (7.2), namely

$$p = p_0(1 + \gamma t). \quad \ldots \ldots \quad (7.3)$$

This expresses **Charles's constant volume law,** viz. *if the volume is kept constant, all gases undergo an increase in pressure equal to 1/273 of their pressure at 0° C. for each degree Centigrade rise of temperature.* The fact that the coefficient of pressure increase is numerically equal to the coefficient of volume increase shows that, on the pressure scale also, the natural zero of temperature would occur at $-273°$ C., for then the pressure as well as the volume would become zero. We represent temperatures on the gas scale by θ, so 0° C. = 273° on the gas scale. In particular, equations (7.2) and (7.3) become

$$v = v_0 \frac{(273 + t)}{273} = \frac{\theta}{\theta_0},$$

or

$$\frac{v}{v_0} = \frac{\theta}{\theta_0}, \quad \ldots \ldots \ldots \quad (7.4)$$

and

$$\frac{p}{p_0} = \frac{\theta}{\theta_0}, \quad \ldots \ldots \ldots \quad (7.5)$$

where θ corresponds to $t°$ C. and θ_0 to 0° C.

On the gas scale, therefore, the volumes and pressures are directly proportional to the temperatures, provided one or the other quantity is kept constant. Now since by Boyle's law, at constant temperature, $pv = $ constant, the only equation expressing that this law and Charles's two laws hold for one and the same gas is

$$pv/\theta = \text{constant.}$$

The value of the constant depends on the kind of gas and on its mass. If, however, the mass is 1 gram-molecule (i.e. μ grams, where μ is the molecular weight of the gas), the constant is the same for all gases. Thus, *for 1 gram-molecule of any gas,* we have the relation

$$pv = R\theta. \quad \ldots \ldots \ldots \quad (7.6)$$

Equation (7.6) is the most important relation in gas phenomena, and is sometimes termed the **Gas Equation**. The **universal** constant **R** is called the **gas constant**. Its value is $83 \cdot 15 \times 10^6$ ergs per gram-molecule.

If the mass of the gas is m grams, and its molecular weight is μ, equation (7.6) is replaced by

$$pv = \frac{m}{\mu}\mathbf{R}\theta. \qquad \qquad (7.7)$$

The student should note that the equation $pv = R\theta$ is frequently used loosely with reference, not to a gram-molecule, but to any mass of the gas, e.g. 1 gram. In this usage, the value of R is not the same as in (7.6) and (7.7).

Of course the gas equation applies strictly only to ideal gases; besides deviating from Boyle's law in the way we have already discussed, real gases also deviate from Charles's laws. Consequently, to represent actual gases with greater accuracy some more complicated expression such as Van der Waals' equation (Chap. X) must be used. From equation (7.7), for a given mass of gas, $pv/\theta = A$, a constant: consequently if pressure, volume and temperature change simultaneously for a gas, we can find p_2, v_2, or θ_2 if we know *two* of these quantities and their initial values (p_1, v_1, θ_1) because

$$\frac{p_1 v_1}{\theta_1} = A = \frac{p_2 v_2}{\theta_2}.$$

3. Constant Volume Thermometer.

The term gas thermometer is usually understood to refer to an instrument of the constant volume type, as shown in fig. 4, and not to the constant pressure type as described in the next section. The standard gas thermometer consists of a cylindrical bulb of platinum-iridium alloy, about 100 cm. long and of capacity about 1 litre. The bulb contains hydrogen, and is placed in the temperature bath with a window for observing the mercury thermometers if the latter are being calibrated against the gas thermometer. A tube leads from the bulb to a manometer containing mercury with which is combined a barometer, so that the total pressure of the gas can be read directly from the manometer. The temperature scale is constructed by immersing the bulb first in melting ice. The mercury is brought back to a constant mark M on the manometer scale for all readings, the corresponding pressure being observed: then any temperature θ is given by the observed pressure p, since

$$\frac{p_0}{273} = \frac{p}{\theta}, \qquad \qquad (7.8)$$

where p_0 is the pressure at $0°$ C. ($=273°$ on the gas scale), and p is the pressure at $\theta°$ on the gas scale.

For accurate values, corrections must be applied for (a) the expansion of the bulb, (b) the existence of a "dead space" in the tube connecting the bulb to the manometer. The gas in this tube is at some temperature intermediate between those of the bulb and the manometer. If

$$V_1 = \text{vol. of bulb at } \theta_1,$$
$$V_2 = \text{vol. of bulb at } \theta_2,$$
$$v_1 = \text{vol. of connecting tube at } \theta_1,$$
$$P_1 = \text{pressure at } \theta_1,$$
$$P_2 = \text{pressure at } \theta_2,$$

we may apply equation (7.7) to the gas in the bulb, and also to the gas in the tube. Since the *total mass* of the gas is constant, we have by addition

$$\frac{P_1 V_1}{\theta_1} + \frac{P_1 v_1}{\theta_1} = \frac{P_2 V_2}{\theta_2} + \frac{P_2 v'}{\theta'}, \quad \dots \quad (7.9)$$
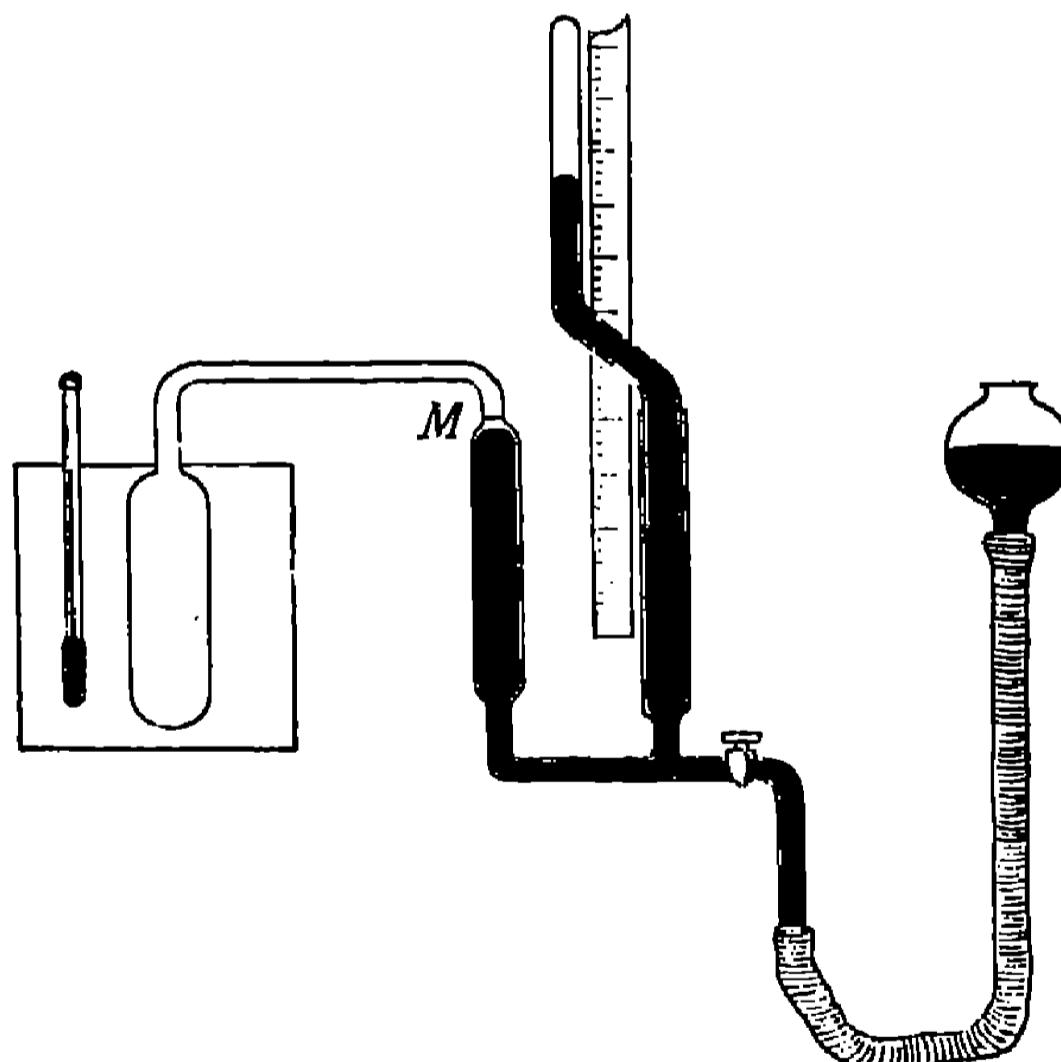
Fig. 4.—Constant Volume Thermometer

where v' corresponds to the volume of the connecting tube at some temperature θ' intermediate between θ_1 and θ_2, which may be defined by

$$\frac{1}{\theta'} = \frac{1}{2}\left(\frac{1}{\theta_1} + \frac{1}{\theta_2}\right). \quad \dots \quad (7.10)$$

In equation (7.9) θ_1 is known if the initial temperature is fixed by immersing the thermometer in melting ice; the desired quantity is

θ_2. Now P_1 and P_2 are measured directly; V_1 and v_1 are known, but V_2 can be calculated only if θ_2 is known, and similarly v' only if θ' is known, which also involves a knowledge of θ_2. Consequently, a method of *successive approximation is used*. Initially V_2 is put equal to V_1 and v' to v_1. Application of equation (7.9) then gives an approximate value of θ_2. Hence (1) an approximate value of V_2 can be calculated, knowing the coefficient of cubical expansion of the container, (2) an approximate value of θ' can be obtained from equation (7.10) and hence an approximate value of v' calculated. Substituting these values in equation (7.9) a new value for θ_2 is obtained. The quantities V_2, θ' and v' are again calculated and resubstituted in equation (7.9) to obtain a still better value of θ_2. Proceeding in this way, after a few successive approximations the value of θ_2 approaches a constant value, which is the true value of θ_2. It is essential that the mercury column should be some distance from the heated bulb, so that variations in the density of the mercury do not occur. The " dead-space " v_1 may be inconveniently large and Callendar and Bottomley inserted a U-tube of concentrated sulphuric acid to act as a buffer and thus reduce the dead-space. The advantages and disadvantages of the gas thermometer are discussed at the end of Chap. I, p. 9.

4. Constant Pressure Thermometer.

A thermometer based on the variation of gas volume at constant pressure is not as accurate as one based upon the variation of pressure
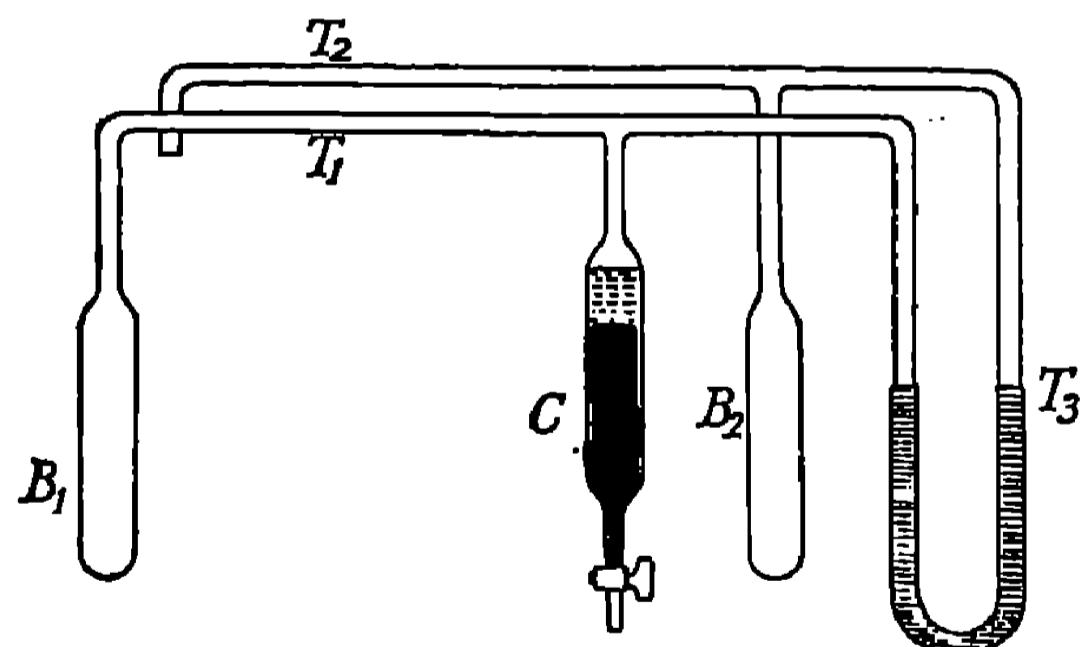
Fig. 5.—Constant Pressure Thermometer

at constant volume. The chief reason is the difficulty of maintaining a continuously increasing volume of gas at constant temperature. In fig. 5 is shown an improved compensating constant-pressure thermometer due to Callendar. The gas is contained in the bulb B_1, and increases in volume are measured, and the pressure maintained constant, by allowing mercury to run out of the graduated container C. The compensating bulb B_2 is equal in volume to B_1 and has a dummy

connecting tube T_2 equal in volume to the connecting tube T_1 and placed beside it. The two bulbs are joined through a U-tube T_3 which contains concentrated sulphuric acid. The whole instrument is first placed in melting ice, and C is filled with mercury. The bulb B_1 is then immersed in the bath at temperature θ and mercury is run out of C until the pressures in B_1 and B_2 are equal as shown by the levels of T_3. If

$$V_1, \ V_1' = \text{vol. of } B_1 \text{ at } \theta_0 \text{ and } \theta \text{ respectively,}$$
$$V_2 = \quad ,, \quad B_2 \ ,, \ \theta_0,$$
$$v_1 = \quad ,, \quad T_1 \ ,, \ \theta_0,$$
$$v_2 = \quad ,, \quad T_2 \ ,, \ \theta_0,$$
$$v_1' = \quad ,, \quad T_1 \text{ at } t \text{ where } \frac{1}{t} = \frac{1}{2}\left(\frac{1}{\theta_0} + \frac{1}{\theta}\right)$$
$$v_2' = \quad ,, \quad T_2 \ ,, \quad ,, \quad ,, \quad ,, \quad ,,$$
$$P = \text{initial pressure in system,}$$
$$P' = \text{final} \quad ,, \quad ,, \quad ,,$$
$$V = \text{vol. of gas expelled into C,}$$

then, by applying equation (7.7) to the two systems as at (7.9),

$$\frac{P'V_1'}{\theta} + \frac{P'v_1'}{t} = \frac{PV}{\theta_0} + \frac{PV_1}{\theta_0} + \frac{Pv_1}{\theta_0}, \quad . \quad . \quad (7.11)$$

and

$$\frac{P'V_2}{\theta_0} + \frac{P'v_2'}{t} = \frac{PV_2}{\theta_0} + \frac{Pv_2}{\theta_0}. \quad . \quad . \quad . \quad (7.12)$$

Now $V_2 = V_1$, $v_2 = v_1$, and $v_2' = v_1'$, since the tubes are similarly placed: hence from (7.11) and (7.12),

$$\frac{\theta}{\theta_0} = \frac{V_1'}{V_1 - V}. \quad . \quad . \quad . \quad . \quad . \quad (7.13)$$

5. Specific Heats of Gases.

If a gas is heated at constant pressure and is therefore allowed to expand, it is found that to produce the same rise in temperature more heat must be supplied than if the gas is heated at constant volume. Representing the specific heat of a gas at constant pressure by c_p and at constant volume by c_v respectively, $c_p > c_v$. We discuss this more fully in Chap. XI and XII; here we state briefly that in the former case external work is done by the expanding gas, and hence heat energy must be supplied to do this as well as to raise the temperature of the gas.

(a) Constant Volume.

The specific heats of gases at constant volume were determined by Joly with the differential steam calorimeter shown in fig. 6. Two

additional scale-pans are suspended from the arms of a delicate balance, and are placed in an enclosure into which steam can be admitted. Two identical copper spheres are taken and placed in each scale-pan, one sphere being completely exhausted and the other filled with the gas whose specific heat is required. To magnify the effect the gas is at a pressure of several atmospheres. The steam condenses on the apparatus, and according to the principles discussed in Chap. VIII the temperature is raised from room temperature to approximately 100 C. by the latent heat given out when the steam condenses. Eventually a steady temperature is reached, and it is found that more water has
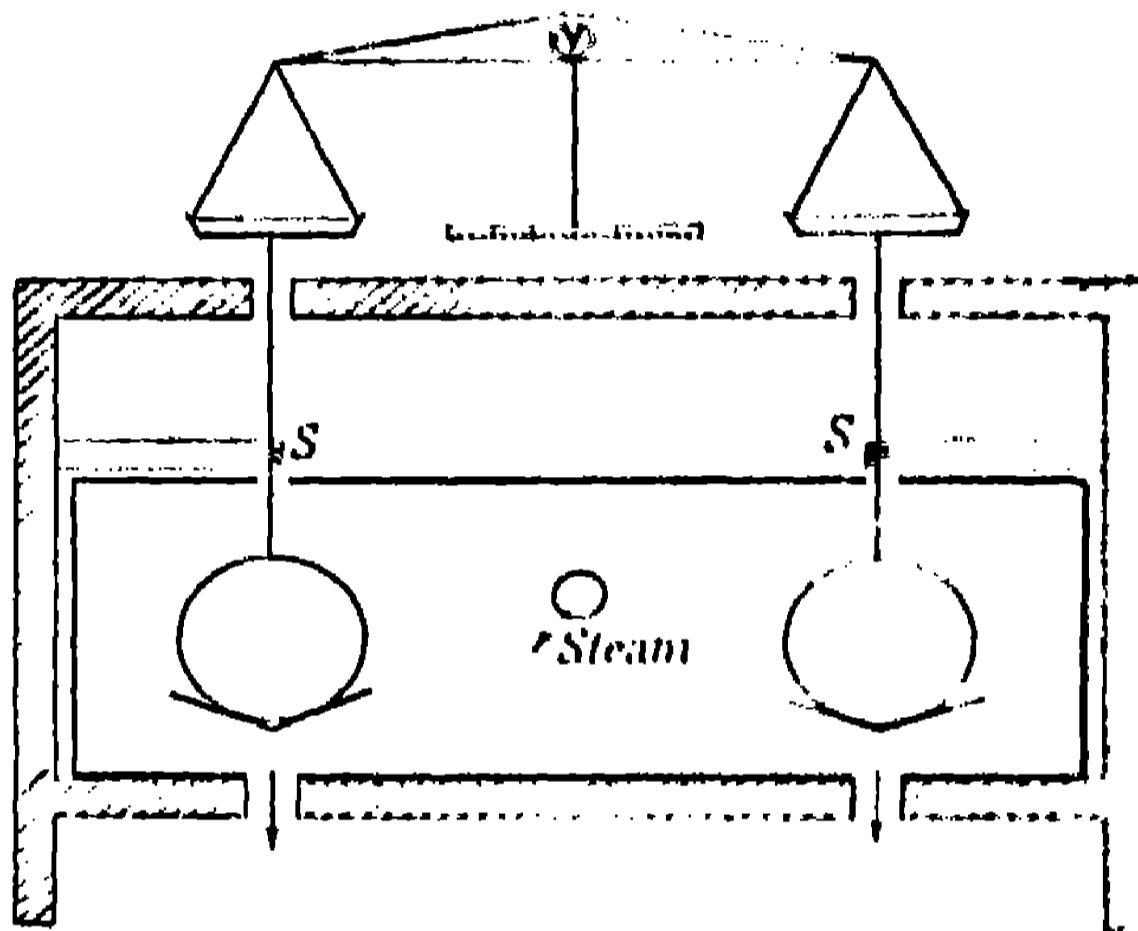
Fig. 6.—Joly's Differential Steam Calorimeter

condensed on the gas-filled sphere than on the evacuated sphere. This is because the former requires heat for raising the temperature of the gas as well as that of the container. The excess weight w of water is determined by calibrating the deflection of the pointer of the balance with a small weight. If

L = latent heat of condensation of steam,
c_v = specific heat of gas at constant volume,
θ = initial temperature of gas,
$100°$ C. = final temperature of gas,
W = mass of gas present,

then $\qquad wL = Wc_v (100 - \theta).$ . . . . (7.14)

Various factors such as the greater expansion of the sphere containing the gas have to be taken into consideration. It is usual to prevent condensation at the small holes through which the suspending wires

pass by encircling them with electrically heated spirals S as shown in fig. 6.

In modern determinations, a *Nernst calorimeter* is used. The detailed description of this apparatus is beyond the scope of this book, but the principle consists in supplying electrically a known quantity of heat to gas in a closed container. The relatively large heat capacity of the container is sometimes reduced by carrying out the experiment at low temperatures, since, as we have seen on p. 33, the specific heat of solids falls rapidly when the temperature is reduced.

(b) Constant Pressure.

In fig. 7 is shown the method due to Regnault; it is simply the method of mixtures adapted to gases. Gas whose pressure is controlled
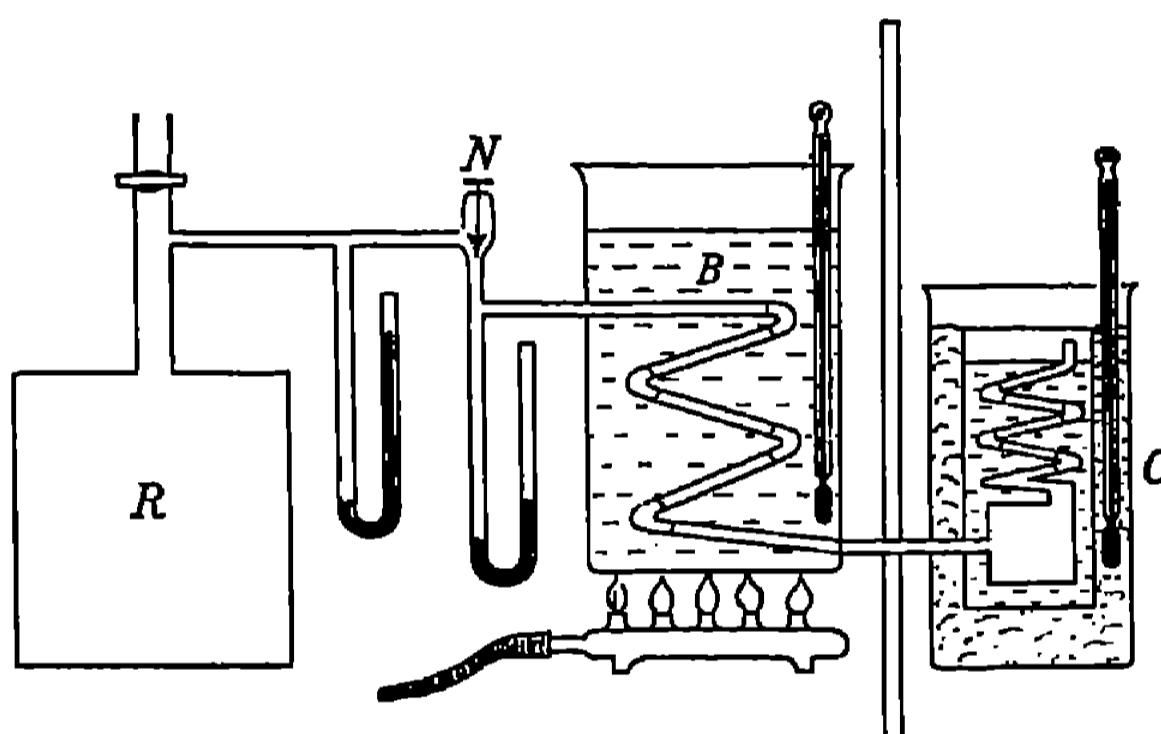
Fig. 7.—Regnault's Constant Pressure Method for c_p

and kept constant by continual adjustment of the needle valve N is allowed to flow from the reservoir R through a spiral immersed in a hot oil bath B, to the calorimeter C. Pressures are read on the manometer; the mass M of gas which has passed is known by reading the pressure of the reservoir before and after the experiment. Application of Boyle's law, together with a knowledge of the density of the gas, allows the mass to be calculated. Then if

θ = temp. gas acquires in oil bath,
θ_1 = initial temp. of calorimeter and contents,
θ_2 = final temp. of calorimeter and contents,
W = water equivalent of calorimeter and contents,

it follows that

$$M.c_p\left(\theta - \frac{\theta_1 + \theta_2}{2}\right) = W(\theta_2 - \theta_1). \quad . \quad . \quad . \quad (7.15)$$

Corrections must, of course, be applied to equation (7.15) to allow for heat losses as in the ordinary method of mixtures.

Modern determinations of the specific heat at constant pressure use the continuous flow method of Callendar and Barnes, already described for liquids on p. 32.

It should be noted that the **ratio γ of the specific heats of a gas at constant pressure and constant volume** occurs in many experiments. Hence if *either* c_p or c_v is known, an experimental determination of the ratio allows the third quantity to be determined. For example, Clement and Désormes' experiment, described on p. 108, allows the determination of γ. Much more accurate is the determination of γ from the velocity of sound in the gas, an experiment described in detail in Part IV.

Finally the student may note that the theory of gases is so well understood that the values of c_p and c_v may be calculated *purely theoretically* from measurements on *band spectra* (see Part III) far more accurately than they can be measured by thermal methods. Even our simple treatment of kinetic theory in Chap. XI gives us a great deal of information about the specific heats of gases.

EXERCISES

1. Describe experiments which have shown the deviations of gases from Boyle's law. What theoretical attempts have been made to account for these departures?

2. In what way do the pressure and volume of a gas vary with temperature on the Centigrade scale? Explain carefully the nature of the gas scale of temperature.

3. Discuss the origin and applicability of the Gas Equation governing the pressure, volume and temperature relations for a perfect gas. Three gases at initial pressures, volumes and temperatures (p_1, V_1, T_1), (p_2, V_2, T_2), and (p_3, V_3, T_3) are allowed to mix in an enclosure at temperature T. If the final pressure in the enclosure is p, what is the volume of the enclosure?

$$\left[\frac{T}{p} \left\{ \frac{p_1 V_1}{T_1} + \frac{p_2 V_2}{T_2} + \frac{p_3 V_3}{T_3} \right\} \right].$$

4. Describe an *accurate* form of gas thermometer, indicating clearly any corrections which may be necessary. How is the effect of the connecting tubes of a constant volume gas thermometer estimated?

5. Give an account of some form of constant pressure thermometer.

Compare the advantages and disadvantages of this instrument with one of constant volume type.

6. If no particular attention is paid to the pressure-volume variations of a gas when it is heated, its specific heat is found to vary from experiment to experiment. Explain this and find an expression for the difference

in the two extreme values of the specific heat in terms of R, the gas constant. $[c_p - c_v = \mathbf{R}/\mu.]$

7. Describe the experimental determination of the specific heats of a gas at constant pressure and constant volume respectively.

8. Given that the specific heat of a gas at constant volume enclosed in one sphere of a Joly differential steam calorimeter is 0·3, find the excess mass of water which will condense on this sphere if its volume is 1000 c.c., its initial and final temperatures 15° C. and 100° C., and the gas is at a density of 8·00 × 10⁻³ gm./c.c. Latent heat of condensation of water = 540 cal./gm. [0·38 gm.]

CHAPTER VIII

Change of State

1. Introduction.

If a mixture of ice and water is heated, it is found that the temperature of the mixture remains constant at 0° C. until all the ice has disappeared. Since heat has been supplied unaccompanied by any rise in temperature, it follows that it has probably been used in changing the state of the material from solid to liquid. Conversely, if heat is abstracted from a mixture of ice and water, no depression of temperature below 0° C., is observed until all the water has solidified. Heat phenomena which accompany change of state are said to be due to **latent heat.** The two laws of **latent heat of fusion** may be stated thus:

I. *For a given pressure, the temperature of fusion of a crystalline mass is fixed and is the same as for solidification. Consequently, while fusion or solidification is taking place, the temperature of the mixture remains constant.*

II. *During fusion, heat is absorbed by the substance, and an equal quantity of heat is evolved by the substance during solidification.*

2. Determination of Melting-points.

If a cooling curve (see Chap. IV) is plotted for water by inserting a thermometer in water contained in a beaker and surrounded by a freezing mixture, its appearance will be as shown in fig. 1. When the freezing-point is reached, heat is evolved according to Law II above; consequently the temperature remains at 0° C. until freezing is complete. The horizontal portion of the curve therefore shows the melting-point or freezing-point. If a substance like paraffin-wax is used, a similar curve is obtained except that the horizontal portion is less well-defined. The melting-point can therefore only be fixed approximately about 52° C. Mixtures or even the presence of small impurities strongly affect the sharpness of definition of the melting-point, and during the preparation of organic compounds their purity is tested by this property.

If only a small quantity of the material is available, it is tapped into a fine glass capillary tube, and the tube is attached directly to the stem of a thermometer by rubber bands. The thermometer is then

immersed in a temperature bath and the temperature is raised very slowly. Melting is indicated by the formation of a few drops of liquid in the capillary tube; the temperature at which this occurs is noted. After all the material has melted it is allowed to cool and the temperature noted at which solid first appears, as indicated by slight opacity. The mean of the temperatures is taken as the melting-point.

In general, only crystalline substances have a definite melting-point, the remainder becoming plastic and melting over a considerable range of temperature. Even crystalline substances may be temporarily **super-cooled**. If great care is taken to avoid disturbances of the liquid and a smooth container is used, it is possible to cool the liquid considerably below its accepted freezing-point. Immediately,
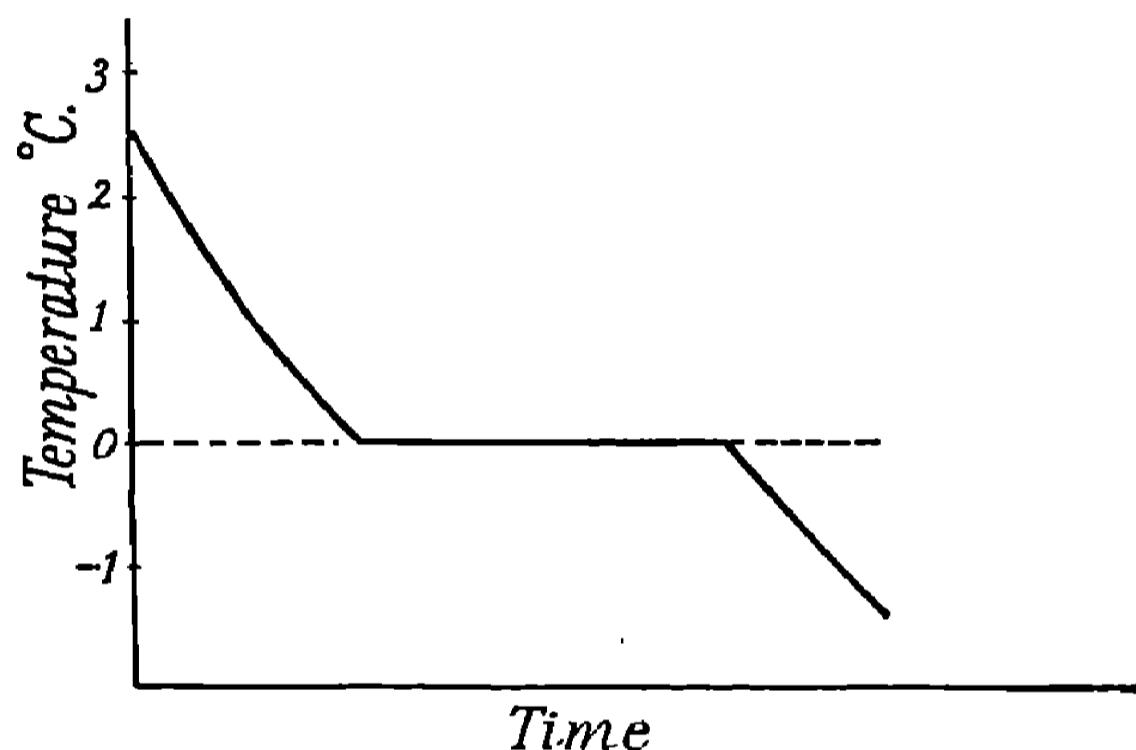
Fig. 1.—Cooling Curve for Water

however, a particle of the solid is formed in or dropped into the super-cooled liquid, the whole mass freezes and the temperature rises to the normal freezing-point owing to the latent heat evolved on solidification. Alloys and mixtures occupy an anomalous position. For example, *Rose's metal*, which consists of an alloy of two parts of bismuth (m.-pt. 271° C.), one part of lead (m.-pt. 327° C.), and one part of tin (m.-pt. 232° C.), melts at 94° C.

3. Effect of Pressure on the Melting-point.

As the temperature is reduced, most liquids contract fairly uniformly in volume. This contraction continues at the change of state, the volume of the solid being less than that of the same mass of liquid. As we have seen in Chap. II, water is an exception in that an expansion occurs when the temperature is reduced below 4° C.: this expansion is continued on solidification, the volume increasing by about 10 per cent. The metals, iron and antimony, also expand on solidification, and they are therefore useful in making sharp casts from a mould. Ordinary molten rock contracts on solidification, and the

process may lead to remarkable results if the molten magma is homogeneous. Thus, the Giant's Causeway on the north-east coast of Ireland exhibits a series of basaltic columns which show almost perfect hexagonal section. The reason for this is that, on contraction, work has to be done against the surface tension forces. The hexagon is the geometrical figure which gives the maximum of area with the minimum of perimeter, together with perfect packing.

The effect of pressure on the melting-point may be easily deduced if it is known whether an increase or a decrease in volume occurs on solidification. If the volume increases, added pressure will tend to prevent the solid forming. Consequently, *the freezing-point of water*
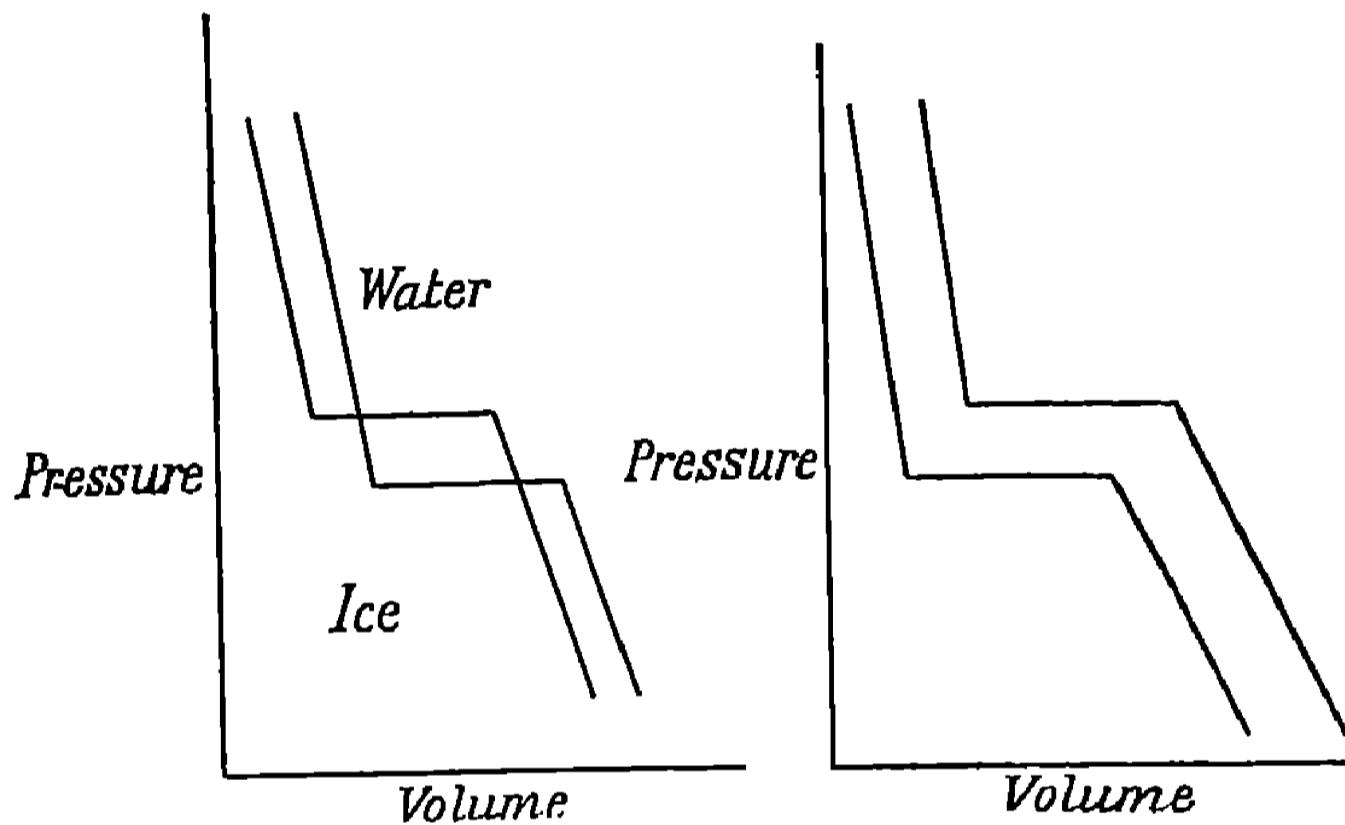
Fig. 2.—Isothermals near Freezing-point: (left) Water; (right) Substance contracting on Freezing

is lowered by a rise in pressure. Strictly speaking, therefore, the pressure must be specified when a melting-point is stated. The depression in freezing-point may be calculated theoretically by the application of thermodynamics as in Chap. XIII. Familiar examples of depression of the freezing-point of ice occur in the making of snowballs, in skating, and in the regelation experiment.

With *snowballs* it is found that the snow will not " bind " under pressure from the hands, if the temperature is much below freezing-point. Binding is due to momentary melting under the increased pressure accompanied by freezing when the pressure is relaxed. If the temperature of the snow is very low, the pressure is insufficient to cause melting.

In *skating*, if the weight of the skater is sufficient to melt the ice, a layer of water is formed beneath the skates and lubrication is good. Since the edge of the skates is fine, the pressure, which is force per unit area, is generally sufficiently great to cause momentary melting.

In the *regelation* experiment two equal weights are attached to a

fine wire and slung across a block of ice so as to hang down on either side of the block. Owing to the pressure the ice beneath the wire melts and the wire goes through. In this way the wire sinks through the block but the block is not permanently divided. When the wire has passed through, the pressure is released, and consequently the water above the wire refreezes.

The isothermals (see Chap. XII) of substances which expand and those which contract on solidification are different, inasmuch as the former intersect each other, while the latter do not, as shown in fig. 2.

4. Behaviour of Solutions.

We saw that with alloys, the melting-point of the alloy was considerably less than that of the constituents. Similarly, solutions in water and other liquids exhibit a *depression in freezing-point* below that of the pure solvent. With substances which do not dissociate (see Part V), the depression in the freezing-point is (*a*) directly proportional to the concentration, (*b*) inversely proportional to the molecular weight of the solute. For further details the student should consult a textbook of Physical Chemistry.

5. Measurement of Latent Heat of Fusion.

The latent heat of fusion is usually determined by the method of mixtures already described for specific heat measurement in Chap. III. For example, a quantity of ice is dried on blotting-paper and added to water contained in a calorimeter, the temperature of which is sufficient to melt all the ice added. The mass m of ice added is determined from the total weight of water present at the end of the experiment. Then if L is the latent heat of fusion, usually expressed in calories per gram,

$$mL + m\theta = W(\theta_1 - \theta), \quad . \quad . \quad . \quad . \quad . \quad (8.1)$$

where θ = final temperature,
θ_1 = initial temperature of calorimeter and contents,
and W = water equivalent of calorimeter and contents.

Radiation corrections must be applied as usual.

If the ice is initially below $0°$ C., an additional term must be added to the L.H.S. of (8.1) to represent the heat required to warm the ice to $0°$ C. The specific heat of a substance may be profoundly changed by change of state, that of ice, for example, being only about 0·5.

If L is known, specific heats may be measured with an **ice-calorimeter**. In *Black's ice-calorimeter*, which is only of historical interest, a cavity in a block of ice was fitted with an ice lid and a known mass of material, previously heated to a known temperature, was dropped

into the cavity. The water formed was removed with a sponge and weighed. The calculation is left to the reader.

A much more delicate apparatus was devised by Bunsen, who used it to determine the specific heat of the rare metal indium. As shown in fig. 3, *Bunsen's ice-calorimeter* consists of a glass test-tube T which fits into a larger tube containing pure distilled air-free water. This is surrounded by an air space, the whole being enclosed in a jacket of melting ice. The latter is in contact with a mercury column C, the end of which moves along a fine capillary tube by the side of a scale. The position of the mercury can be adjusted by manipulation of the screw
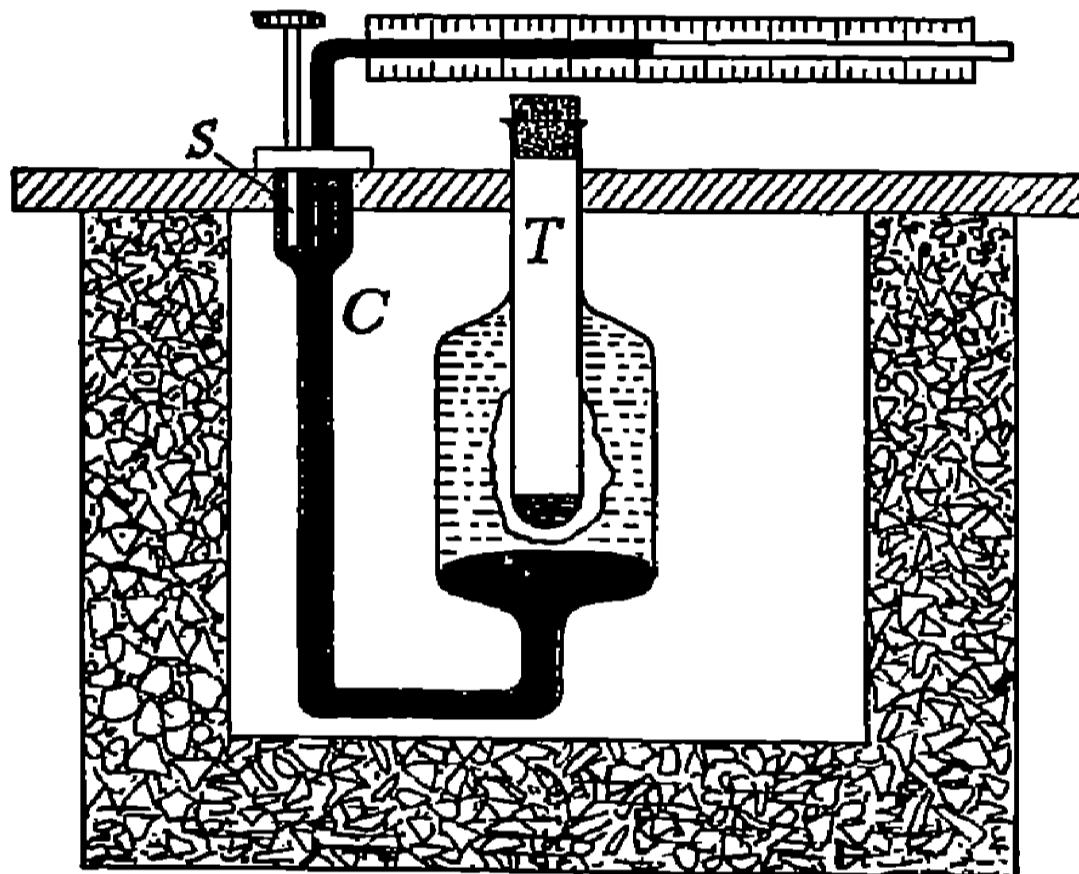
Fig. 3.—Bunsen's Ice Calorimeter

S. Initially, ether is placed in the test-tube and a current of air is blown rapidly through the ether. Owing to the latent heat absorbed in vaporization (see later, p. 73), a crust of ice forms round the test-tube. This ice occupies a larger volume than the water, and the mercury moves along the capillary tube to some new position. As the heat in the room melts the ice, a steady creep is observed along the scale, and allowance must be made for this in estimating the zero readings of the instrument. To calibrate the apparatus, a small mass of water m_1 is introduced into the tube T at a known temperature θ_1, and the contraction d_1 is observed as this water is reduced in temperature by the melting ice to 0° C. If, then, a mass m_2 of the material at temperature θ_2 is introduced and the new contraction is d_2, then

$$m_1(s_1 = 1)\theta_1 = kd_1,$$

and

$$m_2s_2\theta_2 = kd_2,$$

whence

$$s_2 = \frac{d_2}{d_1}\frac{\theta_1}{\theta_2}\frac{m_1}{m_2},$$

where s_2 is the specific heat required, k being a constant of the apparatus which is eliminated by calibration. The radiation losses are included in the correction which is applied for the drifting zero. The disadvantages of the instrument are: (*a*) it is difficult to make and use, (*b*) thermal equilibrium takes a long time to establish itself. It has the advantage of high sensitivity.

6. Latent Heat of Vaporization.

The change of state from liquid to vapour is accompanied by phenomena which bear a general similarity to the transition from solid to liquid. Thus, a thermometer immersed in a boiling liquid shows no elevation of temperature after the boiling-point is reached, the heat being used to effect the change of state. The two laws of vaporization state that:

I. *For a given pressure, the temperature of vaporization is fixed and is the same as for condensation. Consequently, while condensation or boiling is taking place, the temperature remains constant.*

II. *During vaporization, heat is absorbed and an equal quantity of heat is evolved during condensation.*

The latent heat of vaporization is much greater than that of fusion, since the amount of energy which must be given to effect the former change is much greater than for the latter. For example, the latent heat of vaporization of water is about 540 cal./gm. whereas the latent heat of fusion of ice is only about 80 cal./gm.

There are no exceptions to the rule that all substances expand on transition from the liquid to the vapour state. Consequently, since the volume of a given mass of vapour is always greater than the volume of the same mass of liquid, increased pressure favours the liquid state and the boiling-point is always raised. In Chap. XIII we calculate an expression for the elevation in the boiling-point from thermodynamics. The presence of impurities, or of dissolved substances, in the liquid always results in an elevation of the boiling-point. As in the transition from solid to liquid, the change in the fixed point, for a dissolved substance which does not dissociate, is (*a*) proportional to the concentration, (*b*) inversely proportional to the molecular weight of the solute. For further experimental details the student must refer to a textbook of Physical Chemistry.

The change of state from liquid to vapour is discussed more fully in Chaps. IX and X.

7. Ebullition.

Even at low temperatures liquids are always undergoing a certain amount of evaporation, but as the temperature is raised a point is reached when the surface of the liquid is unable to afford the means

of sufficiently rapid escape of the vapour. Bubbles of vapour are then formed in the interior of the liquid, and these throw the liquid into the familiar state of unrest termed boiling or ebullition. If the containing vessel is very clean and smooth, the temperature of a liquid may be raised considerably above its boiling-point without ebullition occurring. This phenomenon of **superheating** is clearly analogous to that of a super-cooled liquid. Dufour made experiments in which drops of water were suspended in oil of cloves and heated to 178° C. without boiling. If boiling commences locally in a superheated liquid, it spreads with explosive violence throughout the liquid, and normal boiling does not set in until the excess heat present has all been removed as latent heat of vaporization. The ease with which vaporization occurs if small rough surfaces are present is well known, and is the reason for adding small pieces of porous pot to the contents of a flask if gentle boiling is desired. Ordinary ether contained in a test-tube will boil momentarily at room temperature if a small ball of paper or a piece of fine wire is inserted into the liquid. The explanation lies in the provision of vaporization nuclei. The dependence on the liquid and on the radius of the nuclei is treated in Chap. IX.

Fig. 4.—Method of Mixtures for Latent Heat

8. Experimental Determination of Latent Heat of Vaporization.

(a) *Method of Mixtures.*

In fig. 4 is shown a modification of the method of mixtures due to Berthelot for the measurement of latent heat of condensation. The liquid is contained in the boiling flask F up the centre of which passes a hollow tube T which conducts the vapour down into the calorimeter C. Then if m is the mass of vapour condensed and L is its latent heat of condensation, an equation similar to (8.1) is directly applicable.

(b) *Electrical Method.*

This method is a modification of the electrical method for specific heat determination described on p. 31. The liquid is heated by an immersed wire spiral to its boiling-point and allowed to boil vigorously. Then if m is the loss in weight due to evaporation and L is the specific heat of the liquid,

$$I^2Rt = mL + \text{heat losses,}$$

where $t = $ time of boiling,

$I = $ current strength,

$R = $ resistance of heating coil.

Suitable correction for heat losses is carried out as in ordinary calorimetry.

EXERCISES

1. Define (a) *latent heat of fusion*, (b) *melting-point of a substance*. What is the effect of (a) external pressure, (b) presence of impurities, on the melting-point of solids?

2. State the Laws of Fusion and describe in detail how the latent heat of fusion of a metal such as lead might be determined.

3. Describe Bunsen's ice-calorimeter and give the theory of its action.

If the mercury recedes 20 divisions when 10 gm. of a substance are cooled from 50° C. to 0° C., find its specific heat, given that the mercury recedes 15 divisions when 20 gm. of copper of specific heat 0·094 are cooled from 100° C. to 0° C. in the same Bunsen ice-calorimeter. [0·501.]

4. A top of moment of inertia 10^4 gm. cm.^{2} rotates about its vertical cylindrical axis on a block of ice, with an initial speed of 1000 revs./min. Assuming that air resistance may be neglected and that the latent heat of fusion of ice is 80 cal./gm., find the depth to which the axis of the top will eventually sink into the ice owing to the heat generated by friction. The top is initially at 0° C., its axis is 1 mm.^{2} in cross-section, and Joule's equivalent is $4 \cdot 2 \times 10^7$ ergs/cal. The density of ice is 0·92 gm./c.c. [1·8 cm.]

5. State the Laws of Vaporization and describe an *accurate* method of measuring the latent heat of condensation of a liquid.

6. Explain the process of ebullition. In what way does the condensation of vapour depend on the presence of electrical charges, and how has this dependence been applied to investigations in atomic physics?

7. A calorimeter contains a liquid immersed in which is a coil of wire carrying a current of 2 amp. under a potential difference of 2·5 volts. After the liquid has been boiling briskly for 4 min., the weight of the liquid is reduced by 5 gm. Find the latent heat of vaporization of the liquid. [57 cal./gm.]

Vapour Pressure, Vapour Density and Hygrometry

1. Vapour Pressure: Statical Measurement.

We have already mentioned that a liquid is always undergoing slow evaporation even when well below its boiling-point. This vapour exerts a definite gas pressure, termed the vapour pressure of the liquid. At ordinary temperatures the vapour pressure may conveniently be measured by introducing a small quantity of the liquid into the Torricellian vacuum of a barometer tube, as shown in fig. 1 (a) (b). The liquid evaporates in the Torricellian vacuum, and the vapour pressure may be read directly from the depression of the mercury in
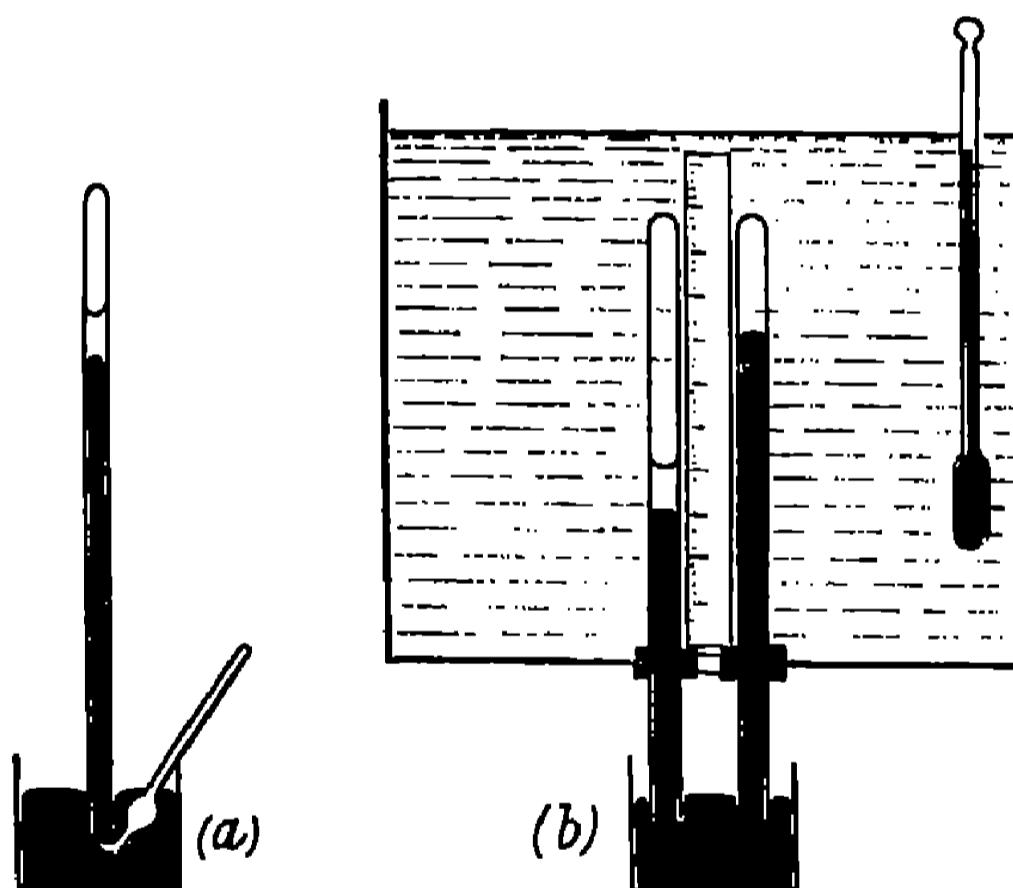
Fig. 1.—Measurement of Vapour Pressure

the barometer tube. As more liquid is introduced, the vapour pressure increases but eventually a layer of unvaporized liquid remains on the mercury. Addition of further liquid fails to increase the observed vapour pressure, which is then said to be the **saturated vapour pressure.** This quantity is characteristic of the material, having a definite value at a definite temperature.

If the tube is surrounded by a water bath and the temperature is raised, the saturated vapour pressure increases as in fig. 2, which shows the variation of the saturation vapour pressure of water with

temperature. Ultimately, the vapour pressure reaches the external atmospheric pressure and at this temperature the liquid is observed to boil. In fact, the best **definition of boiling-point** is *that temperature at which the vapour pressure is equal to the external pressure.*
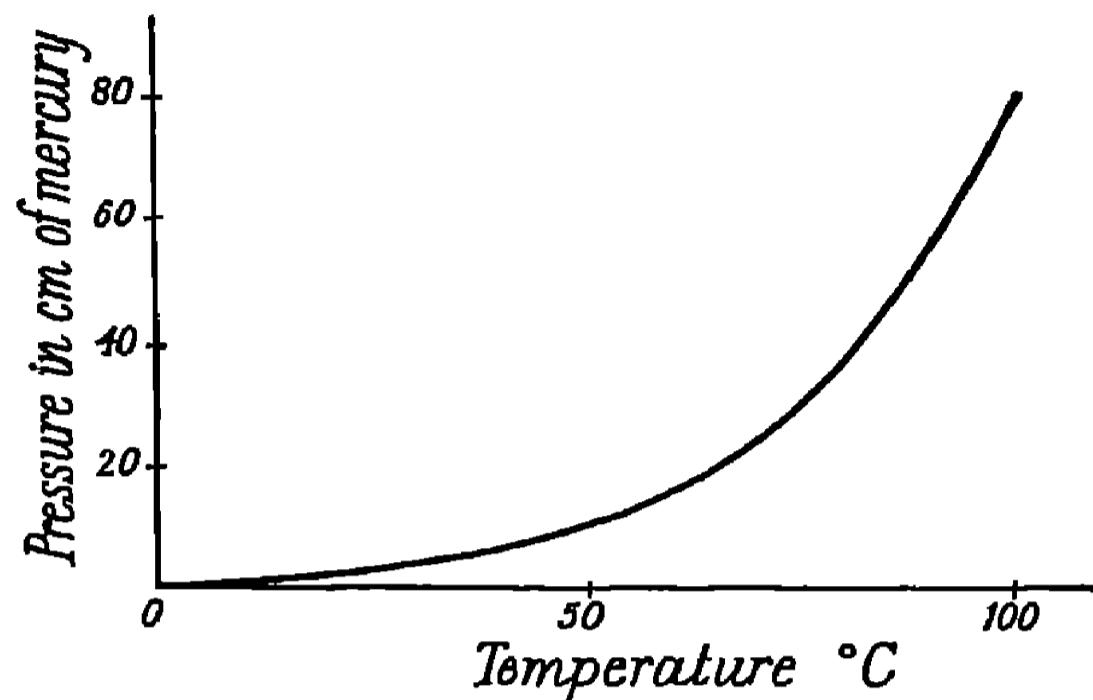
Fig. 2.—Saturation Pressure of Water Vapour

2. Dynamical Method for Vapour Pressure.

The simple statical apparatus already discussed is not suitable for measuring vapour pressures above atmospheric pressure. In fig. 3 is shown an apparatus of the type due to Regnault; it is based on a
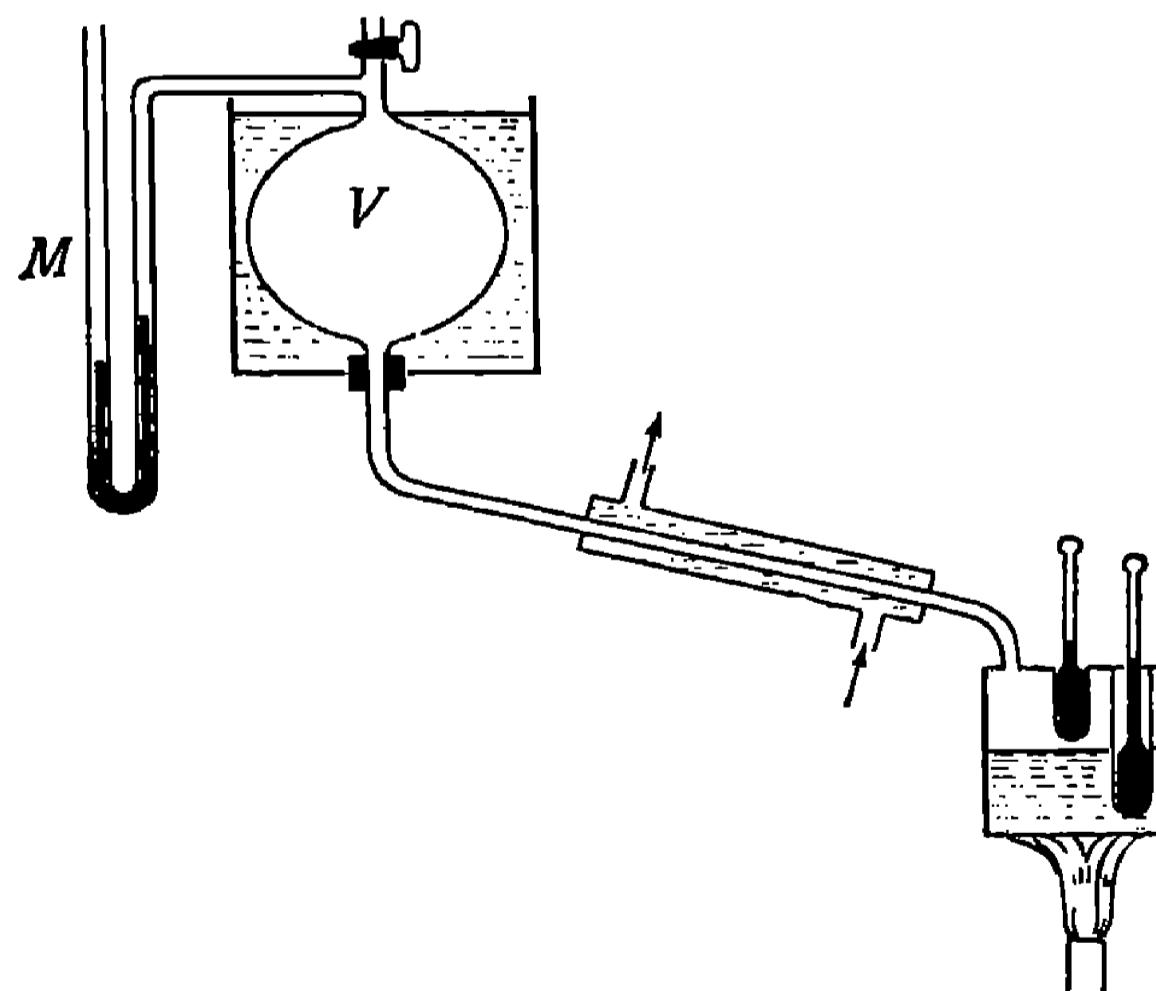
Fig. 3.—Regnault's Apparatus for measuring Vapour Pressure

dynamical principle. The liquid is boiled in a closed reservoir which leads to a Liebig's condenser and a large vessel V. The vessel V communicates with a manometer M, which allows the pressure in the system to be measured. By adjusting the manometer the pressure is

raised to various values and the liquid is then boiled under these different pressures. The thermometers indicate steady boiling-points corresponding to the different external pressures, which, since the system is in equilibrium, must be the vapour pressures corresponding to those temperatures. The large vessel V is a buffer inserted between the boiling vessel and the manometer, to smooth out the violent fluctuations in pressure consequent on boiling.

3. Dalton's Law of Partial Pressures.

Dalton's law of Partial Pressures states that when two or more gases occupy the same vessel then each exerts the pressure which it would exert in the absence of the others provided no chemical interaction is occurring. This law is also applicable to vapours, though it holds only over a limited range, as otherwise an unlimited pressure might be produced by the introduction of a sufficient number of different liquids.

It is instructive to consider the behaviour of vapours and gases in the simple Boyle's law apparatus described in Part I, p. 107. If the gas is mixed with saturated vapour, a condition secured by having a small quantity of liquid always present above the mercury, the vapour pressure remains constant when the volume is altered. Thus, if the pressure due to the vapour is p, and that due to the gas present is p_1, while the external pressure at any instant is P,

$$P = p + p_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.1)$$

But whereas p is constant, p_1 is inversely proportional to the volume at any instant, since the gas obeys Boyle's law. Hence if the gas pressures are p_1 and p_2 at the instants when the volumes are V_1 and V_2,

$$p_1 V_1 = p_2 V_2 = \text{constant}, \quad . \quad . \quad . \quad . \quad (9.2)$$

or from (9.1), if the external pressures are P_1 and P_2,

$$(P_1 - p)V_1 = (P_2 - p)V_2 = \text{constant}, \quad . \quad . \quad . \quad (9.3)$$

and not $P_1 V_1 = P_2 V_2$, as would be the case if there were no saturated vapour present.

On the other hand, if an unsaturated vapour is not too near the condition for condensing it will behave approximately as a perfect gas. For example, a *small* quantity of water vapour introduced into a Boyle's law tube would approximately obey Boyle's law.

4. Vapour Density.

Vapour density is defined as the mass of unit volume of the vapour. It depends on the pressure and temperature of the vapour, and different methods are used for its determination according as the vapour

density is required at ordinary or at high temperatures. We tabulate below various methods which are available:

(a) Gay-Lussac's and Hofmann's methods;
(b) Dumas's method;
(c) Victor Meyer's method.

As vapour densities are often involved in evaluating molecular weights, the subject has been investigated by physical chemists, and the student should consult a textbook of Physical Chemistry.

*5. Effect of Curvature of the Surface on Vapour Pressure.

Reference to Part I, Chap. XI, section 6, shows that when a capillary tube is inserted vertically into a liquid, in many cases the liquid stands in equilibrium above the general level, the curvature of the surface at A in fig. 4 being concave upwards. Now the liquid and its vapour are in equilibrium at A and at B; the pressure across the surface at the former point must clearly be less than that at the latter by an amount equal to σgh where σ is the density of the vapour (assumed constant with height) and h is the height AB. If p is the vapour pressure at B and p' its value at A, then

Fig. 4.—Effect of Curvature on Vapour Pressure

$$p - p' = \sigma gh. \qquad \ldots \ldots \quad (9.4)$$

Now from Part I, Chap. XI, equation (11.5), the pressure just under the curved surface at A is $\left(p' - \dfrac{2T}{r}\right)$, where T is the surface tension of the liquid and r is the radius of curvature of the surface. Hence, if the density of the liquid is ρ, the liquid pressure at B, the bottom of the column, is P where

$$P = \left(p' - \frac{2T}{r} + \rho gh\right). \qquad \ldots \ldots \quad (9.5)$$

Now for equilibrium $P = p$. Hence, from (9.4) and (9.5),

$$\frac{2T}{r} = gh(\rho - \sigma), \qquad \ldots \ldots \ldots \quad (9.6)$$

or, eliminating h,

$$p - p' = \frac{2T}{r} \frac{\sigma}{(\rho - \sigma)}, \qquad \ldots \ldots \quad (9.7)$$

or, representing the difference in vapour pressure over a level and a curved surface by Δp,

$$\Delta p = \frac{2T}{r} \frac{\sigma}{(\rho - \sigma)}. \qquad \cdots \cdots \quad (9.8)$$

If the variation of vapour density σ with the height h is taken into account, it can be shown that equation (9.8) becomes

$$\log_e \frac{p}{p'} = \frac{2T}{r} \frac{\sigma}{p\rho}. \qquad \cdots \cdots \quad (9.9)$$

Consideration of equation (9.8) leads us to important conclusions concerning the processes of evaporation, boiling and condensation. For example, if r is very small, Δp becomes very large. This explains the comparative ease with which fogs occur in dust-laden atmospheres. The dust particles act as nuclei of appreciable radii of curvature; consequently, the supersaturation Δp, due to cooling of the atmosphere laden with water vapour, does not have to be so large as under dust-free conditions. Besides dust-particles, electric charges facilitate the formation of drops, and this fact forms the basis of the Wilson cloud method for examining atomic particles, discussed in Part V.

The student will also now appreciate more fully the process of ebullition discussed in section 7, Chap. VIII. If moderately large pieces of porous pot are present, vapour can form around them as nuclei, and the excess pressure present is of moderate amount since the radii of the nuclei are large. If no, or only very small, nuclei are present, the excess pressure generated when the vapour starts to grow will be extremely large, and the equilibrium between hydrostatic pressure and vapour pressure in the liquid will be very unstable.

6. Hygrometry.

Hygrometry is that branch of physics which relates to the water vapour in the atmosphere.

The **relative humidity** of the atmosphere is defined as

$$\frac{\text{pressure of water vapour actually present}}{\text{saturated vapour pressure of water at the same temperature}} = \frac{p_1}{p_2}. \qquad (9.10)$$

Condensation of water vapour occurs if the vapour pressure rises above the saturation vapour pressure at the given temperature. If, for example, a beaker is cooled by passing a current of air through ether contained in the beaker, at a certain stage of the cooling dew will form on the beaker. The temperature of the beaker at which this occurs is termed the **dew-point**. The dew-point is therefore the temperature at which the actual vapour pressure in the atmosphere is the

saturation vapour pressure. The condensation of water which is easily seen on mirrors, spectacles, &c., when they are suddenly introduced into a warm room is simply due to the cooling of the air and water vapour in contact with the cold object. The actual pressure of water vapour in the room is greater than the saturation vapour pressure at the temperature of the mirror, and condensation therefore occurs on the latter.

Solids as well as liquids exert a vapour pressure. Sometimes, as in the case of " dry ice " or solid carbon dioxide, the vapour pressure is so large that, on heating, the substance passes directly into the vapour state (or *sublimes*), without passing through the liquid stage at all. To a lesser extent snow and ice evaporate directly and, in the formation of hoar-frost, water vapour passes directly into the solid state without liquefying in the process.

Most hygrometers depend upon the measurement of the dew-point for the determination of the relative humidity. From previously constructed tables showing the variation of the saturation vapour pressures of water with temperature, the pressures p_1 and p_2 appropriate to t_1 and t_2, the temperatures of the dew-point and of the room respectively, are obtained directly.

(a) Regnault's Hygrometer.

In this apparatus, as shown in fig. 5, two identical glass tubes have metal thimbles attached to the bottom and hold thermometers T_1 and T_2. One of the tubes is cooled by drawing air through ether contained in the tube. The other thermometer remains at room temperature. The observer notes the dew-point, that is, the temperature at which dew collects on the cold thimble, taking care, by interposing a sheet of glass between his breath and the thimble, not to add to the humidity of the air.

(b) Wet and Dry Bulb Hygrometer.

This hygrometer has the advantage of great simplicity, and is therefore widely used in meteorology. Two thermometers are mounted side by

Fig. 5.—Regnault's Hygrometer

side; around the stem of one is wound a piece of cotton waste which dips into a small vessel containing water. Owing to the continuous evaporation from the cotton waste, the wet bulb shows an appreciably lower reading than the dry bulb. Empirical tables are constructed connecting the dew-point with the difference in reading
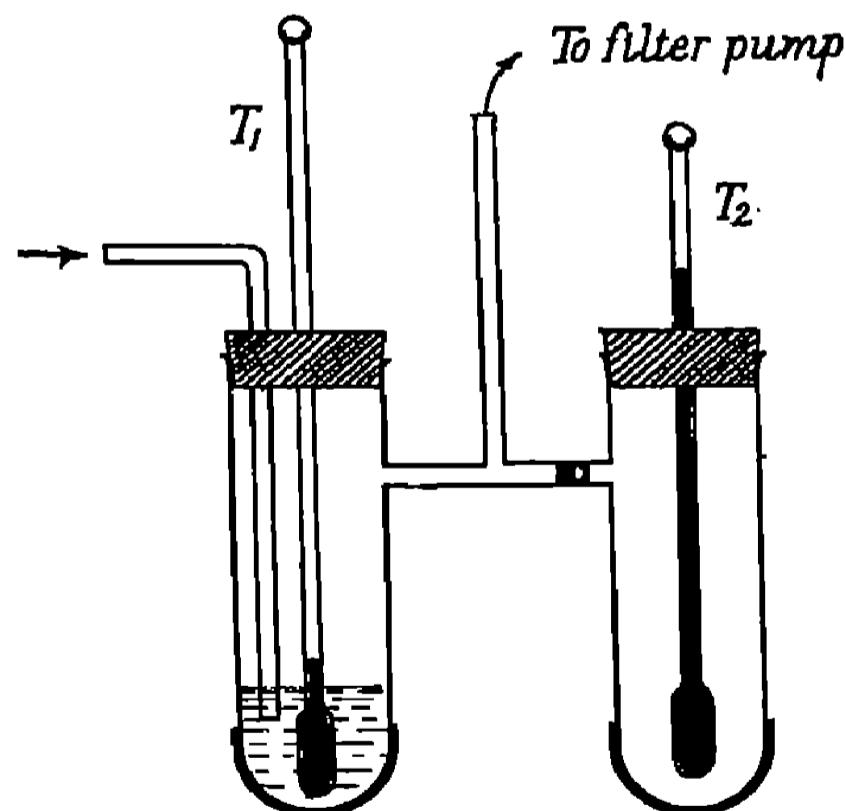
of the wet and dry bulbs, and hence the relative humidity is obtained. An approximate theoretical treatment is as follows:

P = pressure of water vapour in the air,
p = saturation vapour pressure at temp. of wet bulb,
t = temp. of dry bulb,
t' = temp. of wet bulb.

The air over the wet bulb becomes saturated, and its vapour pressure therefore rises from P to p, and latent heat is taken up proportional to this rise, say $A(p - P)$. This heat comes from the wet bulb, which is cooled through $(t - t')$, and the heat given up is proportional to this, say $B(t - t')$. Hence

$$A(p - P) = B(t - t').$$

Actually, $P = p - 0.011(t - t')$ when the barometer is about 29·4 in., and the relation is valid for a moderate range of pressure round this value.

(c) *Chemical Hygrometer.*

Since the density of the vapour is approximately proportional to the vapour pressure, an alternative definition of relative humidity is

$$\frac{\text{mass of water vapour actually present (per c.c.)}}{\text{mass of water vapour present (per c.c.), if saturated}}$$

On this definition is based the chemical hygrometer shown in fig. 6. A given volume of air is drawn through a weighed drying tube T_1 by
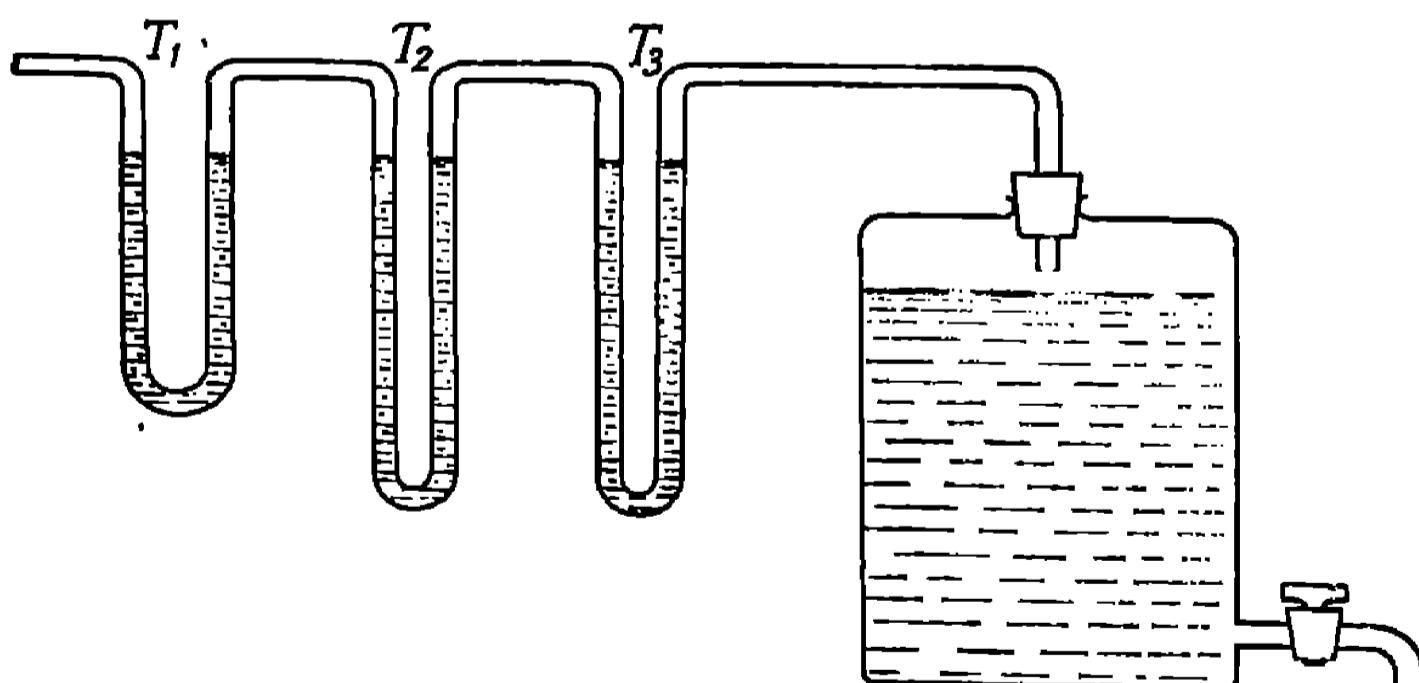
Fig. 6.—Chemical Hygrometer

means of an aspirator. Connected to T_1 are two additional tubes T_2 and T_3; the former absorbs any water vapour which has failed to be caught in T_1; the tube T_3 prevents water vapour from the aspirator from reaching the weighing tubes. The method is accurate but cumbersome.

(d) *Hygroscopes.*

Changes in humidity may be registered automatically by instruments termed hygroscopes, an example of which is shown in fig. 7. They depend for their action on the fact that the human hair or other fibre changes in length when a variation occurs in the humidity of the atmosphere. The small change in length is magnified by suitable levers to operate a pointer moving over a calibrated scale.
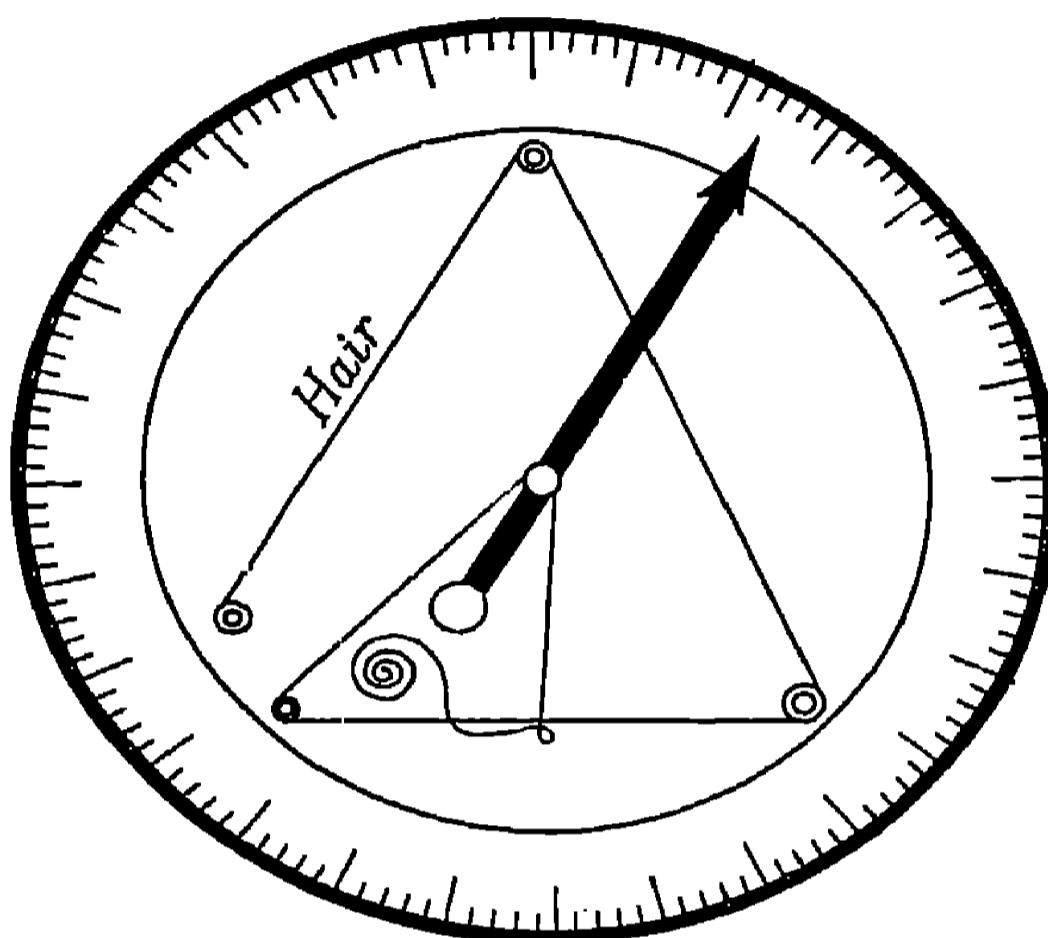
Fig. 7.—Hygroscope

EXERCISES

1. Describe statical and dynamical methods for measuring the vapour pressure of liquids at different temperatures, indicating the conditions under which each method is applicable.

2. State Dalton's Law of Partial Pressures.

The space above the mercury in a simple Boyle's law apparatus contains some air and saturated vapour. If the volume of the space is doubled when the external pressure is reduced from 76 cm. to 50 cm. of mercury, find the vapour pressure of the liquid. [24 cm.]

3. Explain clearly what is meant by *unsaturated* and *saturated vapour pressure* of a liquid.

Find the volume occupied by dry gas at N.T.P. if 500 c.c. of the gas are subject to an initial pressure of 75 cm. of mercury at 15° C., and are situated over a liquid whose saturation vapour pressure at this temperature is 18 mm. of mercury. [456·5 c.c.]

4. Enumerate methods for finding the vapour densities of substances and describe one method in detail.

Of what particular importance is a knowledge of vapour density for the theory of physics and chemistry?

5. Define the term *relative humidity,* and describe the use of a reliable instrument for determining the hygrometric state of the atmosphere.

CHAPTER X

Continuity of State and Liquefaction of Gases

1. Continuity of State.

It was shown by Cagniard de la Tour that if a liquid is heated in a closed vessel, then, above a certain temperature, the meniscus which normally divides the liquid surface from the vapour disappears. The liquid and vapour states are said to have become continuous, and the temperature at which the merge occurs is termed the **critical temperature.** If the pressure-volume curves are drawn for a substance such as carbon dioxide, the appearance is as in fig. 1. These curves were originally obtained by Andrews and are said to be the isothermals (see p. 104), since each curve shows the appropriate (p-v) relation for constant temperature. Taking the isothermal for $21 \cdot 5°$ C., we see that when the volume is very large and the vapour therefore far from its condensation point, the vapour obeys Boyle's law, as shown by the approximately hyperbolic shape of the curve. As the pressure is increased the vapour eventually liquefies and a sudden contraction in volume takes place, represented by the horizontal portion of the curve. Since liquids are only slightly compressible, further increase in pressure results in an almost vertical line for the (p-v) relation.
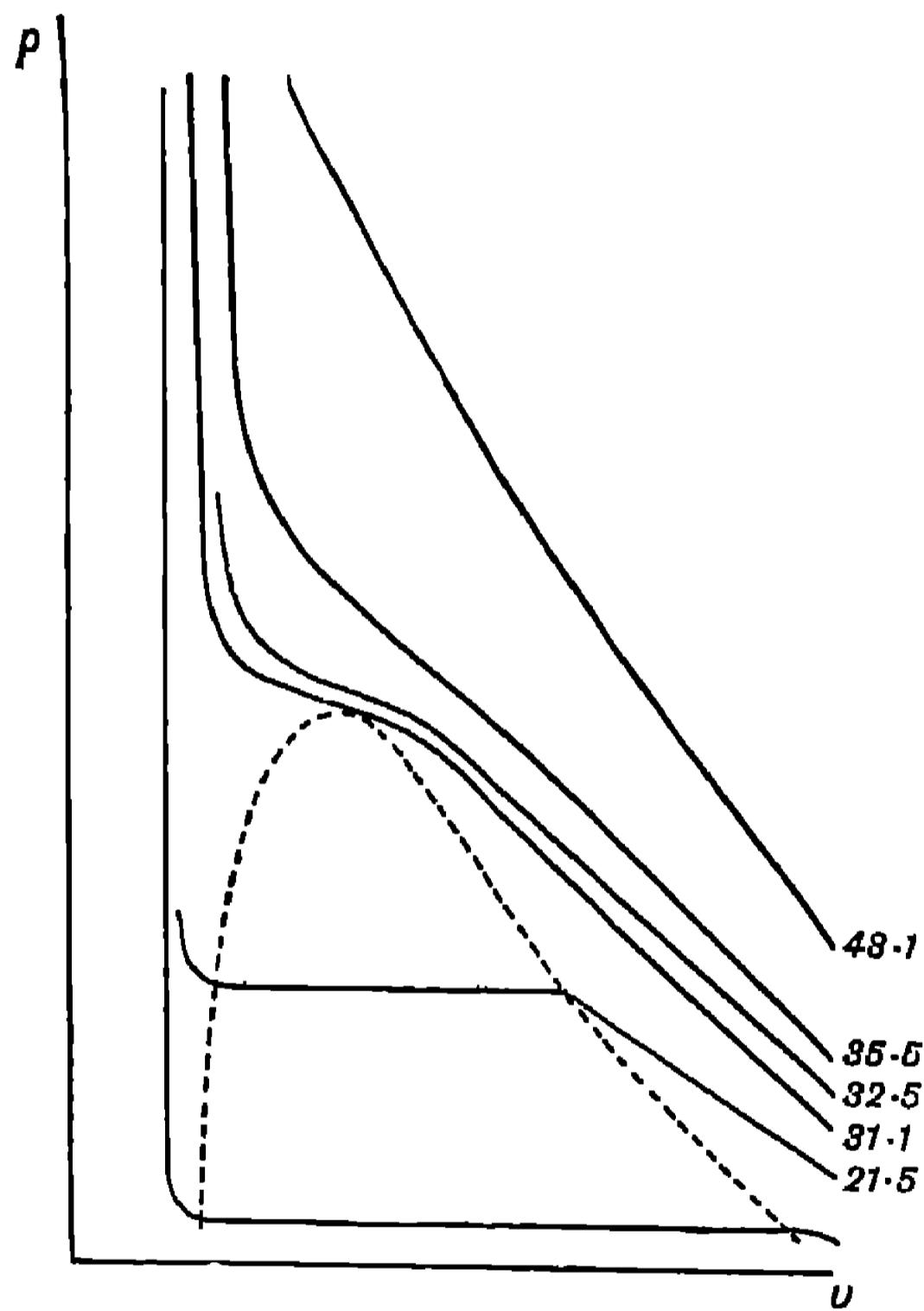
If, however, we consider the isothermal for 48·1° C., we find that

Fig. 1.—Isothermals of Carbon Dioxide

48·1
35·5
32·5
31·1
21·5

84

the curve approximately obeys Boyle's law even up to the highest pressures; no transition to the liquid state takes place. Investigation of intermediate isothermals shows that between 15° C. and 31° C. the horizontal portion indicating the transition from vapour to liquid grows shorter and shorter while it vanishes completely at about 31° C. This temperature is the critical temperature of carbon dioxide. We may therefore take as an alternative definition: **critical temperature is the temperature above which a gas cannot be liquefied simply by increasing the pressure.**

If a curve is drawn between the **transition points,** as shown in the dotted line in fig. 1, this dotted curve just touches the isothermal for 31° C., the latter exhibiting a point of inflexion at this point. The values p_c and v_0 at this point of inflexion are said to be the **critical pressure** and **critical volume** of the substance, and the isothermal at 31° C. is termed the **critical isothermal.**

The term gas is usually reserved for substances above their critical temperatures, and the term vapour for the same substances below that temperature. Carbon dioxide is therefore a gas above 31° C. and a vapour below 31° C. " Permanent " gases like nitrogen and hydrogen are simply substances which at room temperature are much above their critical temperatures. They

Fig. 2.—Andrews's Apparatus

become vapours when they are below their critical temperatures (—147° C. for nitrogen, —240° C. for hydrogen).

The apparatus used by Andrews in obtaining the isothermals for carbon dioxide is shown in fig. 2. The substance was compressed in a fine capillary tube which was surrounded by a water bath. The pressure was supplied by a screw working into a reservoir as in Despretz's experiments on the deviations from Boyle's law (see p. 56). Great care had to be taken to eliminate air from the carbon dioxide tube by working with a current of pure carbon dioxide over a long period before sealing the tube.

2. Van der Waals' Equation of State.

Since the liquid and vapour states are essentially continuous, a more general equation than Boyle's law is required to cover the complete field of phenomena. Such an equation was proposed by Van der Waals on the kinetic theory of gases: we give a deduction in Chap. XI. Briefly, we may state here that a real gas differs from an ideal gas in two particulars:

(a) When a gas "occupies" a volume v, the space in which the molecules are free to move is less than v owing to the volume occupied by the molecules themselves; if we represent this occupied volume by b, the effective volume is reduced to $(v - b)$.
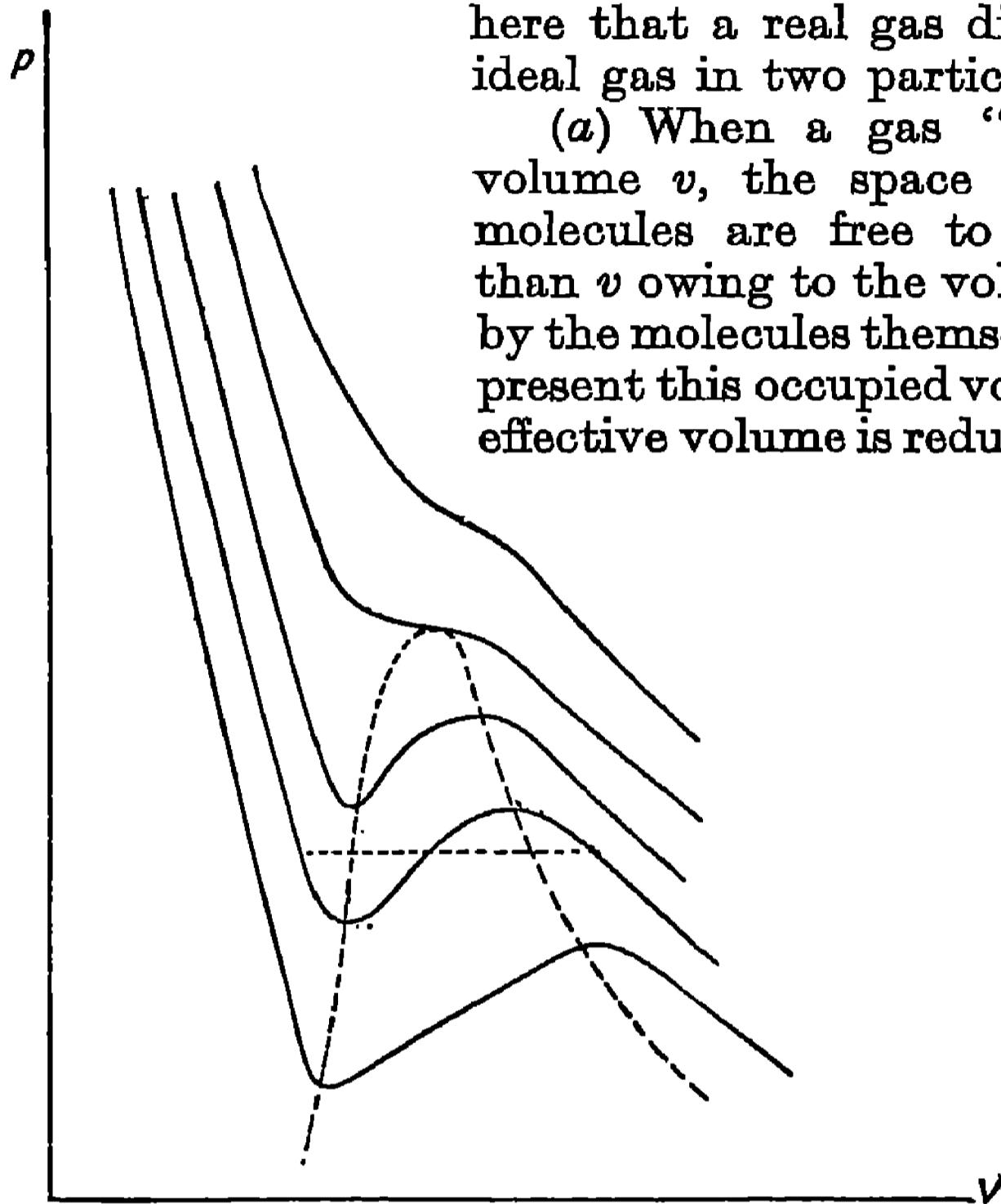
Fig. 3.—Isothermals according to Van der Waals' Equation

(b) The molecules exert a mutually attractive force on each other. This will be greater, the greater the density ρ of the gas. If we imagine two layers of gas attracting each other, the force of attraction will be proportional to the product ρ^2. For a fixed mass of gas the density is inversely proportional to the volume, so the force may be represented by a/v^2, where a is a constant. Now this will tend to reduce the volume just as if the external pressure had been increased. Consequently, the gas equation for an ideal gas must be changed from $pv = R\theta$ to

$$\left(p + \frac{a}{v^2}\right)(v - b) = R\theta. \quad \ldots \ldots \quad (10.1)$$

Equation (10.1) is a cubic in v, and when plotted gives a curve as shown in fig. 3. It will be observed that the general shape of this curve agrees very well with the shape of the experimental isothermals except that the straight, horizontal portion of the latter is replaced by an oscillation as shown. It is now believed that the experimental curve also follows this humped course, but at the transition point from vapour to liquid the experimental conditions become so unstable that it is impossible to examine the situation in detail. Consequently, the change appears as an abrupt transition in the experimental curve. Other comparisons of Van der Waals' equation with experiment will now be given.

We propose to find expressions for p_c, v_c and θ_c in terms of the **Van der Waals' constants**, a and b. The condition for finding v_c is obtained from Van der Waals' equation by noting that v_c occurs at a point of inflexion on the critical isothermal. Consequently, we differentiate Van der Waals' equation twice with respect to v and equate to zero:

$$p = \frac{R\theta}{(v-b)} - \frac{a}{v^2},$$

$$\frac{\partial p}{\partial v} = 0 = -\frac{R\theta}{(v-b)^2} + \frac{2a}{v^3}, \quad \cdot \quad \cdot \quad \cdot \quad (10.2)$$

and

$$\frac{\partial^2 p}{\partial v^2} = 0 = \frac{2R\theta}{(v-b)^3} - \frac{6a}{v^4}. \quad \cdot \quad \cdot \quad \cdot \quad (10.3)$$

Elimination of θ between equations (10.2) and (10.3) gives $v_c = 3b$, and resubstitution gives $p_c = a/27b^2$ and $\theta_c = 8a/27Rb$. Hence, according to Van der Waals' equation, for all gases the ratio $p_c v_c / R\theta_c = 3/8$. This relation is only in approximate agreement with experiment. Again, in Chap. XI, we shall see that the expression $v_c = 4b$ is more nearly true than $v_c = 3b$. On the whole, however, Van der Waals' equation is as satisfactory as any of the other equations of state which have been proposed. Of these we shall only mention the *equation of Dieterici*, namely,

$$p(v-b) = R\theta \exp(-a/R\theta v), \quad \cdot \quad \cdot \quad \cdot \quad (10.4)$$

where a is a constant.

3. Joule-Thomson Experiment.

If a gas is allowed to expand, then, as shown in Chap. XII, it does external work. Besides this *external* work, however, it also does *internal* work. This follows from considerations of the correction introduced in the first term of Van der Waals' equation. The term a/v^2 was inserted to account for the mutual attraction between the molecules. If a gas is allowed to expand, its density decreases and the molecules

in the expanded state are, on the average, a greater distance a; than before the expansion took place. Now energy must have l consumed to do the work of separating the molecules against t mutual attraction. This energy is abstracted from the heat en of the gas and consequently, even when no *external* work is don gas cools slightly on expansion. Joule carried out an experimen test this suggestion, but the results were negative owing to the in sitivity of the apparatus. Later, Kelvin carried out the **porous** **experiment**, which gave a positive result. The gas was allowe stream from a region of high density on one side of a porous plu a region of low density on the other. Thermometers inserted in suit positions showed that a cooling occurred in all cases examined ex hydrogen. If the experiment is carried out below —80° C., hydr also cools on expansion. In fact, there is a definite temperatur all gases, below which they cool on expansion and above which heat. This temperature is termed the **inversion temperature**, ar as important a characteristic of the gas as its critical temperatu

4. Liquefaction of Gases.

(a) *Cascade or Pictet Process.*

It was Faraday who first liquefied what had hitherto been acce as one of the permanent gases. The apparatus was extremely sir consisting of a bent closed tube as shown in fig. 4. At one end chl
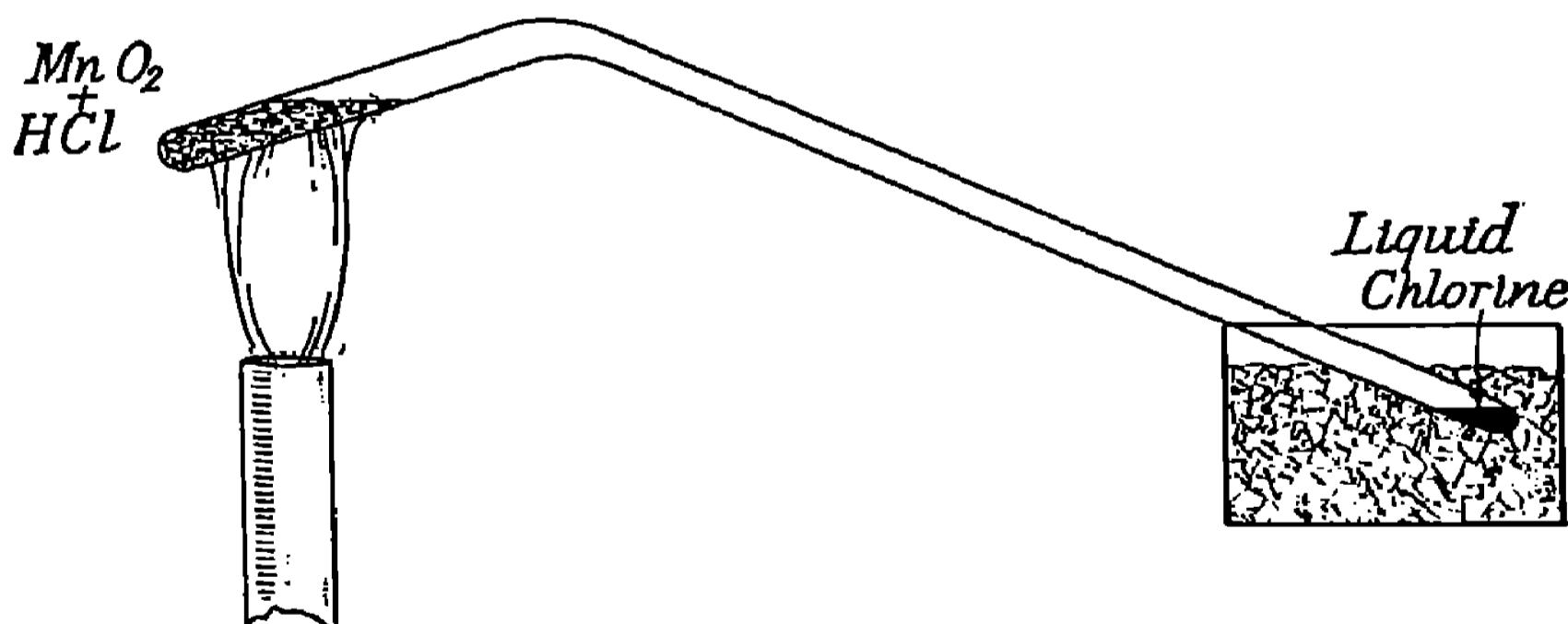
Fig. 4.—Faraday's Liquefaction Experiment

was generated by heating manganese dioxide and hydrochloric while the other end was immersed in a freezing mixture. Sinc critical temperature of chlorine is about 146° C., when the pressi the tube became moderately high, liquid chlorine was formed a cold end. One general process for the liquefaction of gases the consists in cooling the gas below its critical temperature and

applying sufficient pressure. To take a definite case, we consider the production of liquid oxygen. The critical temperature of oxygen is about —118° C.; it cannot therefore be liquefied by compression at ordinary temperatures. The method used is termed the cascade or Pictet process. First, some gas such as methyl chloride whose critical temperature is well above room temperature is liquefied by compression. If the liquid is poured into a Dewar flask (see Chap. XIV), it will evaporate comparatively slowly even if the pressure above the liquid is reduced to one atmosphere. This is because heat cannot reach the liquid, and latent heat of vaporization must be supplied for the liquid to evaporate.

If, now, a second vessel containing another gas, say ethylene, is immersed in the liquid methyl chloride, heat will be abstracted from the vessel and the ethylene by the methyl chloride, some of which will now evaporate. The ethylene is thereby cooled to about —30° C., and since its critical temperature is about +10° C., the ethylene in its turn may now be easily liquefied by compression. Continuing in this way, the liquefied ethylene boiling at atmospheric pressure will abstract heat from an immersed vessel containing oxygen, reducing the temperature of the latter to about —160° C., which is well below its critical temperature. The oxygen may now be liquefied by compression.

The production of liquid air may be carried out by a similar process, since nitrogen has a critical temperature of —146° C. As the liquid air boils off it becomes richer in oxygen since the nitrogen boils off more easily.

(b) Linde-Joule Process.

The previous method involved the conception of the critical temperature. The Linde-Joule process involves the conception of the inversion temperature. The apparatus is shown in fig. 5. Gas at high pressure, and cooled by previous passage through tubes immersed in calcium chloride solution at about —30° C., passes down a spiral which terminates in a very fine nozzle. The gas expands through this orifice

Fig. 5.—Linde-Joule Process

into an outer vessel, the gas pressure in which is kept low by pumping the gas away and returning it to the compressors for repassage through the spiral. The gas cools slightly on expansion, as in the Joule-Thomson porous plug experiment, and this cooled gas sweeps back over the outside of the spiral. Consequently, it cools the down-coming gas, and the whole process is regenerative, the temperature of the gas
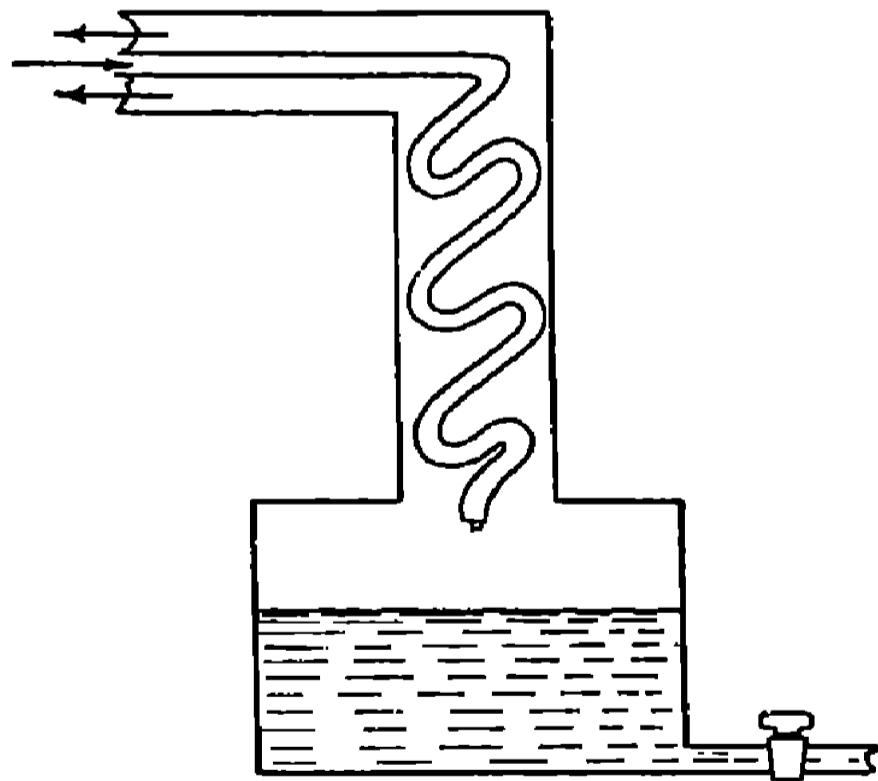
becoming lower and lower until it eventually liquefies and is drawn off from the base of the apparatus.

It is not possible to produce liquid hydrogen or liquid helium by the cascade process since their critical temperatures are below the lowest temperatures reached by the boiling gases which would precede them in the cascade process. They can, however, be liquefied by the Linde-Joule process if their temperatures are first reduced below their inversion temperatures. Since the inversion temperatures of gases are always much higher than their critical temperatures, there is no difficulty in the initial cooling of hydrogen and helium in preparation for the Linde-Joule process.

5. Production of Low Temperatures.

The history of the production of low temperatures is of considerable interest. In 1898, Dewar used the Linde-Joule process to produce liquid hydrogen. Ten years later, Onnes succeeded in liquefying the last remaining gas, helium, by the same process. With helium boiling under reduced pressure a temperature of $-272°$ C. was eventually produced, but still the liquid helium did not freeze. It was not until 1926 that Keesom succeeded in producing solid helium. The transition from liquid to solid is usually observed by placing the liquid inside a nest of transparent Dewar flasks, the outer flasks containing liquefied gases of higher boiling-point. Thus the liquid helium was surrounded by flasks of liquid hydrogen and liquid air. On freezing, a change in the refractive index is usually observed, but in the case of helium the refractive index of liquid and solid helium is almost the same. Eventually a metal stirrer which could be operated magnetically from outside was installed, and sticking of the stirrer indicated the freezing of the helium.

Temperatures which are within a fraction of the absolute zero may now be obtained by first cooling with liquid helium and then demagnetizing certain crystals adiabatically (see Chap. XII). Magnetic energy leaves the system and the temperature is reduced to less than $0·01°$ absolute.

EXERCISES

1. Explain clearly what is meant by the term *continuity of state* as applied to liquids and gases.

How has the gas equation for perfect gases to be modified?

2. Define *critical temperature* as applied to the liquid-vapour transition of a substance. Describe the experiments of Andrews on the critical temperature of carbon dioxide.

3. What equations have been proposed to replace the equation of state for perfect gases and how far are they in agreement with experiment?

4. Give an account of the liquefaction of gases by the cascade process. How would you measure the boiling-point of liquid oxygen boiling steadily in a vacuum flask at atmospheric pressure?

5. Describe and give the theory of the Joule-Kelvin porous plug experiment. How have the ideas been applied to the liquefaction of gases on a large scale?

6. Write a short essay on the production and measurement of low temperatures.

7. Show that, under certain conditions, Dieterici's equation of state reduces to that proposed by Van der Waals.

8. Prove that for all gases $p_c V_c/RT_c = 3/8$ if Van der Waals' equation is obeyed, p_c, V_c, T_c being the critical pressure, volume and temperature of a gas, and R the gas constant referred to a gram-molecule.

9. Explain the difference between critical temperature and inversion temperature. Upon which concept is the liquefaction of hydrogen and helium based?

CHAPTER XI

Kinetic Theory of Gases

1. Introduction.

Since all gases obey, at least approximately, the simple gas laws of Boyle and Charles, it is reasonable to suppose that they all possess a common and simple structure. It was suggested first by Bernoulli that the pressure of a gas could be explained if the molecules, of which the gas is composed according to chemical theory, were endowed with considerable translational velocity. Bernoulli actually deduced Boyle's law, but it was not until Joule carried out in 1848 his classical work on the equivalence of mechanical work and heat that the kinetic theory could expand and assume its present comprehensive form.

In 1857, Clausius formulated the following basic postulates for a kinetic theory of gases:

(a) The molecules of a given monatomic gaseous element are regarded as identical solid spheres which move in straight lines until they collide with one another or with the wall of the containing vessel.

(b) The time occupied in collision is negligible; the collision is perfectly elastic, and there are no forces of attraction or repulsion between the molecules themselves.

(c) The molecules are negligible in size compared with the size of the container.

Clausius also introduced the important conception of the **mean free path** of a gas molecule; it is defined as the average distance traversed by a molecule between successive collisions. The quantities required for a knowledge of the properties and condition of a gas are (1) the velocity of the molecules, (2) the mean free path at S.T.P. (standard temperature and pressure), (3) the number of molecules per unit volume at S.T.P., (4) the diameter of a gas molecule regarded as a hard elastic sphere.

2. The Gas Laws and Avogadro's Hypothesis.

Consider a cubical volume of side l containing n gas molecules. Then if V_1 is the velocity of any one molecule and m is its mass, its momentum is mV_1. If this molecule strikes the face ABCD in fig. 1, it communicates a force to the face, but the only component of velocity

which is effective is the component normal to the face. Calling this component u_1 and the other two components at right angles to it and to each other v_1 and w_1, then

$$V_1{}^2 = u_1{}^2 + v_1{}^2 + w_1{}^2. \quad . \quad . \quad . \quad . \quad (11.1)$$

If the collision is perfectly elastic, the molecule rebounds with velocity V_1, and consequently the component momentum of recoil in a direction perpendicular to ABCD is $-mu_1$.

Hence the change in momentum produced by impact is $mu_1 - (-mu_1) = 2mu_1$ perpendicular to ABCD. After recoil, if the direction of impact was almost normal to the surface, the molecule will travel to the opposite face, collide with it and rebound again to the face ABCD, the time between the successive collisions on ABCD being $2l/u_1$. Hence the average number of collisions per second which this molecule makes with ABCD is $u_1/2l$, and the average rate of change of momentum is

Fig. 1.—Components of Velocity

$2mu_1 . u_1/2l = mu_1{}^2/l$. For some other molecule with velocity V_2 and components u_2, v_2 and w_2, the change of momentum per second due to impact with ABCD will be $mu_2{}^2/l$.

Now by Newton's Second Law of Motion

Rate of Change of momentum ≡ impressed force,

so the force on ABCD is

$$F_x = \frac{m}{l}(u_1{}^2 + u_2{}^2 + u_3{}^2 + \ldots u_n{}^2).$$

Since pressure is force per unit area, the average pressure on ABCD due to the molecular bombardment is

$$p_x = \frac{F_x}{A} = \frac{F_x}{l^2} = \frac{m}{l^3}(u_1{}^2 + u_2{}^2 + u_3{}^2 + \ldots u_n{}^2). \quad (11.2)$$

Similarly, if p_y and p_z represent the pressures on the faces of the cube, perpendicular to the y- and z-axes respectively,

$$p_y = \frac{m}{l^3}(v_1{}^2 + v_2{}^2 + v_3{}^2 + \ldots v_n{}^2), \quad . \quad . \quad (11.3)$$

$$p_z = \frac{m}{l^3}(w_1{}^2 + w_2{}^2 + w_3{}^2 + \ldots w_n{}^2). \quad . \quad (11.4)$$

Hence the average pressure p produced by the gas is

$$p = \frac{p_x + p_y + p_s}{3} = \frac{m}{3l^3}\{(u_1{}^2 + v_1{}^2 + w_1{}^2) + (u_2{}^2 + v_2{}^2 + w_2{}^2) +$$

$$\ldots (u_n{}^2 + v_n{}^2 + w_n{}^2)\}. \quad . \quad . \quad . \quad . \quad (11.5)$$

Now $l^3 = v =$ volume of cube, and substituting also from equation (11.1), equation (11.5) becomes

$$pv = \tfrac{1}{3}m(V_1{}^2 + V_2{}^2 + V_3{}^2 + \ldots V_n{}^2). \quad . \quad . \quad (11.6)$$

Now the **mean square velocity** of the molecules V^2 is defined by

$$V^2 = \frac{(V_1{}^2 + V_2{}^2 + V_3{}^2 + \ldots V_n{}^2)}{n}. \quad . \quad . \quad (11.7)$$

Hence (11.6) may be written

$$pv = \tfrac{1}{3}nmV^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (11.8)$$

or alternatively, $\qquad\qquad p = \tfrac{1}{3}\rho V^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (11.9)$

where $\rho = nm/v =$ density of the gas.

Now it is reasonable to assume, from the equivalence of heat and energy, that the energy of the molecules is a measure of the temperature θ of the gas, that is,

$$\tfrac{1}{2}nmV^2 = C\theta, \quad . \quad . \quad . \quad . \quad . \quad (11.10)$$

where C is some constant of proportionality. Hence, from (11.8) and (11.10),

$$pv = R\theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad (11.11)$$

where $R = \tfrac{2}{3}C =$ constant, which is the *Gas Equation* obtained by combining Boyle's and Charles' laws as on p. 59.

To deduce **Avogadro's hypothesis** that, at the same temperature and pressure, equal volumes of different gases contain the same number of molecules, we have to make the further assumption, which can be proved by complicated mathematical analysis, that the average kinetic energy of the molecules of two different gases is the same when they are at the same temperature. Expressed mathematically, this is written

$$\tfrac{1}{2}m_1V_1{}^2 = \tfrac{1}{2}m_2V_2{}^2. \quad . \quad . \quad . \quad . \quad (11.12)$$

Since p and V are the same for both gases, (11.8) and (11.12) give

$$n_1 = n_2,$$

which is Avogadro's hypothesis.

Equation (11.9) allows us to determine the root mean square velocity for a gas molecule directly, viz.

$$V = \sqrt{\frac{3p}{\rho}}. \qquad \ldots \ldots \quad (11.13)$$

For hydrogen at S.T.P. this velocity is about 10^5 cm./sec.

3. Specific Heats of Gases on Kinetic Theory.

If we consider a gram-molecule of the gas, then equation (11.8) becomes

$$pv = \tfrac{1}{3}MV^2, \qquad \ldots \ldots \quad (11.14)$$

where $M = nm =$ molecular weight of the gas. Now the kinetic energy of the gas $E = \tfrac{1}{2}MV^2$. Hence, from (11.14)

$$pv = \tfrac{2}{3}E. \qquad \ldots \ldots \ldots \quad (11.15)$$

But $pv = R\theta$, so from (11.15)

$$E = \tfrac{3}{2}R\theta, \qquad \ldots \ldots \ldots \quad (11.16)$$

where R refers to a gram-molecule. This equation allows us to define *the gas constant R as $\tfrac{2}{3}$ of the kinetic energy of a gram-molecule of gas at one degree absolute.*

If the gas is heated through $1°$, its energy becomes

$$E_1 = \tfrac{3}{2}R(\theta + 1). \qquad \ldots \ldots \quad (11.17)$$

Now the heat required to raise one gram-molecule of the gas one degree is the **molecular heat** of the gas, where molecular heat = specific heat $\times$ molecular weight. Further, if all the energy is assumed to go to raising the kinetic energy of the molecules and none is used in doing external work, it is the molecular heat at constant volume C_v which is involved. Hence

$$C_v = E_1 - E = \tfrac{3}{2}R, \qquad \ldots \ldots \quad (11.18)$$

an equation which shows that the molecular heat of a gas at constant volume is $\tfrac{3}{2}$ (the gas constant).

We show, in Chap. XII, that

$$C_p - C_v = R. \qquad \ldots \ldots \ldots \quad (11.19)$$

Hence, from (11.18) and (11.19)

$$C_p = \tfrac{5}{2}R, \qquad \ldots \ldots \ldots \quad (11.20)$$

and from (11.20) and (11.18)

$$C_p/C_v = \gamma = \tfrac{5}{3}. \qquad \ldots \ldots \quad (11.21)$$

According to the kinetic theory, therefore, the ratio of the specific

heats of monatomic gases is constant and equal to 5/3. This is in good agreement with experiment for such monatomic gases as helium, neon and the other rare gases.

It may be shown that for diatomic and polyatomic gases the ratio of the specific heats should be progressively less, approaching unity for high atomicity of the molecule. This is also found experimentally.

*4. Mean Free Path and Molecular Radius.

In order to account for the deviations of gases from the ideal gas laws it is necessary, as we saw in developing Van der Waals' equation on p. 86, to take into account the finite size of the molecules. Let s be the diameter of a molecule; then this quantity represents the closest distance to which two molecular centres can approach. To simplify
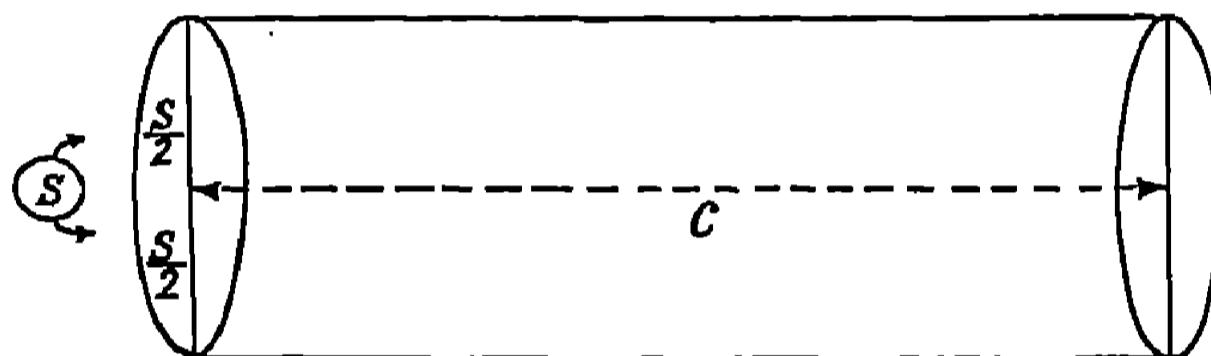
Fig. 2.—Molecular Collisions

calculations, let us endow one particular molecule with an **effective radius** s, treating the others as points. We proceed to calculate an expression for the average number of collisions made by this molecule in one second. If c is the velocity of the molecule, it sweeps out an effective cylindrical volume (fig. 2), per second, equal to $\pi s^2 c$. Hence, if there are ν molecules per unit volume, the number of collisions n per second is

$$n = \pi s^2 c \nu. \qquad \ldots \ldots \quad (11.22)$$

Now the average distance between successive collisions is the mean free path λ: hence the effective distance traversed by the molecule per second is $n\lambda = \pi s^2 c \nu \lambda$. But the distance traversed by the molecule per second is its velocity c. Hence

$$c = \pi s^2 c \nu \lambda,$$

or

$$\lambda = \frac{1}{\pi s^2 \nu}, \qquad \ldots \ldots \ldots \quad (11.23)$$

an important equation deduced by Clausius, connecting the mean free path λ, the molecular diameter s and the number of molecules ν per unit volume.

*5. Viscosity of Gases on the Kinetic Theory.

If we consider a unit cube situated in a gas, then the average number of molecules moving towards any one face of the cube at any instant will be $\nu/6$, where ν is the total number of molecules in the cube. The total number of molecules passing through one face of the cube per second is therefore $\nu c/6$, where c is the average velocity of the molecules. Referring to fig. 3, Chap. XII, Part I, p. 133, let us consider the molecules crossing unit area of a plane drawn parallel to and a distance x from the fixed surface, where the velocity of drift of the gas is v. The molecules which cross from below will have a lower drift velocity than those from above. They will, of course, have the same gas kinetic velocity since the whole gas is at uniform temperature. Consequently there is a net transfer of drift momentum across the area, and by Newton's Second Law this change in momentum will be equal to the viscous force F, where

$$F = \eta \frac{dv}{dx}, \qquad . \quad . \quad . \quad . \quad . \quad (11.24)$$

η being the coefficient of viscosity and dv/dx the velocity gradient as discussed on p. 133, Part I. Now of the molecules which start moving towards the area at x, only those which on the average are not farther away than the mean free path will cross the area. We therefore assume that the mean velocity of the molecules crossing from below is $\left(v - \lambda \frac{dv}{dx}\right)$, and of those from above $\left(v + \lambda \frac{dv}{dx}\right)$. Hence the net transfer of momentum per second is

$$G = \frac{mc\nu}{6}\left\{\left(v + \lambda \frac{dv}{dx}\right) - \left(v - \lambda \frac{dv}{dx}\right)\right\}$$

$$= \tfrac{1}{3}\nu m c \lambda \frac{dv}{dx}. \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11.25)$$

From (11.24) and (11.25),

$$\eta = \tfrac{1}{3}\nu m c \lambda,$$

or

$$\eta = \tfrac{1}{3}\rho c \lambda, \qquad . \quad . \quad . \quad . \quad . \quad . \quad (11.26)$$

where ρ is the density, for ν is the number of molecules per unit volume, since we are considering transfer across unit area.

Now from equation (11.23) $\lambda \propto 1/\rho$, and since c is dependent only on the temperature, according to equation (11.26) **the viscosity η is independent of the pressure.** This law was first deduced by Maxwell, who proceeded to show that it was obeyed experimentally. The apparatus consisted of a flat disk suspended from a torsion wire and allowed to undergo torsional oscillations close to a parallel flat plate. The

pressure of the surrounding gas was changed, but no change in the rate of damping of the oscillating disk occurred, indicating that the viscosity was independent of the pressure. Now in equation (11.26) η may be measured experimentally as in Chap. XII, Part I, ρ is easily determined, and the average velocity c can be shown theoretically to be equal to $(8/3\pi)^{\frac{1}{2}}V$, where V is the root mean square velocity which can be calculated from (11.13). Hence λ may be determined from (11.26), and in this way Maxwell showed that for hydrogen at S.T.P. λ is about 2×10^{-5} cm.

*6. Thermal Conductivity of Gases from Kinetic Theory.

If we have contiguous layers of gas at different temperatures, there will be a net transfer of heat due to the gas-kinetic motion of molecules. By a similar argument to that used in the preceding section, we take the temperature to be θ and the temperature gradient $d\theta/dx$ at some layer x from a given boundary. Then the net transfer of heat per second across unit area of the layer x will be

$$Q = \frac{\nu c}{6} m c_v \left\{ \left(\theta - \lambda \frac{d\theta}{dx} \right) - \left(\theta + \lambda \frac{d\theta}{dx} \right) \right\}$$

$$= -\tfrac{1}{3} \nu m c \lambda \frac{d\theta}{dx} c_v, \quad \ldots \ldots \ldots \quad (11.27)$$

where c_v is the specific heat at constant volume.

Now by our definition of the coefficient of thermal conductivity in equation (5.1)

$$Q = -k \frac{d\theta}{dx}. \quad \ldots \ldots \ldots \quad (11.28)$$

Hence, from (11.27) and (11.28),

$$k = \tfrac{1}{3} \nu m c \lambda c_v$$

$$= \tfrac{1}{3} \rho c \lambda c_v. \quad \ldots \ldots \ldots \quad (11.29)$$

The thermal conductivity of a gas is therefore also independent of the pressure. At *low* pressures, however, both the viscosity and the thermal conductivity of gases are proportional to the pressure, and this relation forms the basis of some low-pressure gauges. The behaviour of gases at low pressures can receive very satisfactory treatment on kinetic theory, but it is beyond the scope of this book.

From equations (11.26) and (11.29), we deduce

$$k = \eta c_v, \quad \ldots \ldots \ldots \quad (11.30)$$

a relation which shows the great generality of the kinetic theory, for it connects the diverse physical phenomena of heat conduction, specific heat and viscosity.

We have now described methods for evaluating V and λ; it remains to describe how the two remaining fundamental quantities, ν the number of gas molecules per unit volume at S.T.P., and s the molecular diameter, are determined. By equation (11.23), if one of these quantities is known, then the other may be calculated.

The number of molecules ν *per unit volume* at S.T.P. is correctly termed **Loschmidt's number**; its value is $2 \cdot 69 \times 10^{19}$. **Avogadro's number** N is the number of molecules *in a gram-molecule*. Since a gram-molecule of any gas occupies $22 \cdot 4 \times 10^3$ c.c., it follows that Avogadro's number $= 2 \cdot 69 \times 10^{19} \times 22 \cdot 4 \times 10^3 = 6 \cdot 06 \times 10^{23}$. The name Avogadro's number is often applied to both numbers. The best method for determining N requires a knowledge of electricity. After studying Part V, the student will realize that

$$N = \frac{Q}{e}, \quad \ldots \ldots \ldots \quad (11.31)$$

where Q is the charge given up to an electrode during electrolysis, by a gram-molecule of a monovalent ion, and e is the charge on that ion, which is the electronic charge. However, we describe in the next section a method of finding N, which, although it is not as accurate as the electrical method, provides an elegant example of the application of kinetic theory.

*7. Brownian Movement.

In 1827, a botanist named Brown observed that if pollen grains about 10^{-3} mm. diameter were in suspension in a liquid, then examination with a microscope showed the pollen grains to be in incessant random motion. Initially the phenomenon was ascribed to vital forces, but subsequent work showed that it was also exhibited by small particles held in suspension in the liquid inclusions in granite and other rocks of great age. Not until nearly fifty years after its discovery was it suggested that the Brownian movement is a visible demonstration of the validity of the kinetic theory of liquids. In any small interval of time, a particle will receive more impacts from molecular bombardment on one side than another. If the particle is sufficiently small, it will therefore execute a small motion under the resultant force until its path is altered by further impacts. The essential feature from the point of view of the kinetic theory is that the particles will be sharing the average kinetic energy of the liquid molecules at the particular temperature under consideration. The particles may therefore be considered to represent visibly the molecular motion of gas molecules, the particles being regarded as molecules of gigantic size.

Now the equilibrium of the atmosphere on the earth's surface is due to two opposing forces, gravitational attraction downwards and

gas pressure upwards. Only a few molecules succeed in reaching the upper regions against the gravitational attraction, and therefore the density decreases rapidly with height. In exactly the same way, if a tube containing small particles in suspension is examined with a microscope, there is seen to be a *sedimentation equilibrium*, most of the particles clustering at the bottom of the tube but a certain number reaching higher regions. The particular particles at any one horizontal layer are continually changing, but after the liquid has been undisturbed for some time, on the average the number present per layer remains constant. In fig. 3, if ν is the number of particles per unit volume at a height h above the bottom of the container, and p the particle-bombardment-pressure on the section at height h, then

if equilibrium has been reached, the small extra pressure $(-dp)$ must balance the weight of the particles in the height dh. Hence

$$dp = -\nu mg\, dh, \quad . \quad (11.32)$$

where m is the *reduced* mass of one particle (that is, its weight in air less the buoyancy in the surrounding fluid), and g is the acceleration due to gravity. Now if we treat the particles as a perfect gas they must obey the Gas Equation, namely,

$$pv = R\theta,$$
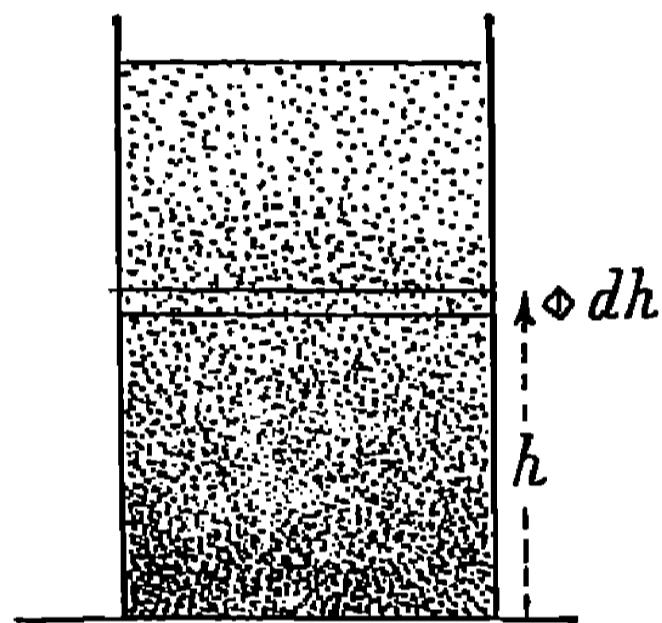
Fig. 3.—Particles in Suspension

where R refers to a gram-molecule. The pressure which such a gas would exert if all the N molecules in a gram-molecule were compressed into *unit* volume would be

$$P = R\theta. \quad . \quad . \quad . \quad . \quad . \quad . \quad (11.33)$$

For the particles in suspension, the pressure is p when the number of particles per unit volume is ν. Hence

$$P/p = N/\nu. \quad . \quad . \quad . \quad . \quad . \quad (11.34)$$

From (11.33) and (11.34),

$$p = \frac{\nu R\theta}{N}. \quad . \quad . \quad . \quad . \quad . \quad (11.35)$$

If we differentiate (11.35) to find the variation of p with ν, we obtain

$$dp = d\nu \frac{R\theta}{N}. \quad . \quad . \quad . \quad . \quad . \quad (11.36)$$

Eliminating dp from (11.32) and (11.36), we get

$$\frac{d\nu}{\nu} = -\frac{mgN}{R\theta}\, dh. \quad . \quad . \quad . \quad . \quad (11.37)$$

From (11.37), by integration, if ν_1 and ν_2 are the numbers of particles per unit volume at heights h_1 and h_2,

$$\log_e \frac{\nu_2}{\nu_1} = -\frac{mg}{R\theta} N(h_2 - h_1), \quad . \quad . \quad . \quad . \quad (11.38)$$

an equation from which N may be determined.

To evaluate N, Perrin used particles of gamboge in water. A drop of the emulsion, centrifuged to obtain particles of one size only, was placed on a microscope slide so as to form a column about 1/10 mm. high, which was then observed with a powerful microscope. Owing to the high power of the microscope, the thickness of the layer in focus was about that of the diameter of the particles: consequently only the number present in a very thin layer was observed for one position of the microscope. The microscope was then racked up a distance d measured on an accurately graduated vernier and another count was made, the distance $(h_2 - h_1)$ being equal to μd, where μ is the refractive index of the emulsion. (See Part III, on real and apparent depth.) The mass of the grains m in equation (11.38) was determined by finding:

(a) the density of the gamboge;

(b) the volume of the grains, obtained by noting their rates of fall through the solution and applying Stokes's law (see Part I and Part V). The viscosity of the solution had to be determined separately. From observations of many thousands of grains, the final value $N = 6\cdot8 \times 10^{23}$ molecules per gram-molecule was obtained. The electronic method gives the now accepted value of $6\cdot06 \times 10^{23}$ mol./gm. mol. Moderately good values of N have also been obtained by observation of Brownian movement of fine particles suspended in gases. Indeed, very small drops in Millikan's experiment (see Part V) are difficult to keep in focus owing to wandering due to Brownian movement.

*8. Van der Waals' Equation and Kinetic Theory.

To deduce Van der Waals' equation from the kinetic theory we consider first the effect of the finite size of the molecules. Since two molecular centres cannot approach closer than the molecular diameter s, if a molecule makes n collisions per second, its effective distance of action in this time is $c + ns$ instead of simply c. Actually such an increased distance of action would only occur if all the molecular collisions were head on. Taking into account that some are only glancing collisions, the effective distance covered may be shown to be $(c + \frac{2}{3}ns)$. The effect of the molecular diameter is to change

(11.9) to

$$p = \tfrac{1}{3}\rho V^2 \frac{(c + \tfrac{2}{3}ns)}{c}, \text{ approx.}$$

$$= \tfrac{1}{3}\rho V^2 \Big(1 + \tfrac{2}{3}\frac{ns}{V}\Big), \quad . \quad . \quad . \quad . \quad (11.39)$$

where c is put equal to V.

Substituting for n from (11.22),

$$p = \tfrac{1}{3}\rho V^2(1 + \tfrac{2}{3}\pi s^3 \nu)$$
$$= \tfrac{1}{3}\rho V^2(1 + \tfrac{4}{6}\pi s^3 \nu).$$

Since $\tfrac{4}{6}\pi s^3 \nu <\!< 1$, this may be written approximately

$$p(1 - \tfrac{4}{6}\pi s^3 \nu) = \tfrac{1}{3}\rho V^2,$$

or

$$pv(1 - \tfrac{4}{6}\pi s^3 \nu) = \frac{M}{3} V^2, \quad . \quad . \quad . \quad . \quad (11.40)$$

where the total mass of gas is M.

Now the volume of ν spheres of radius $s/2$ is $\tfrac{1}{6}\pi s^3 \nu = d$. Hence equation (11.40) becomes

$$pv(1 - 4d) = \frac{M}{3} V^2,$$

or

$$p(v - b) = \frac{M}{3} V^2, \quad . \quad . \quad . \quad . \quad . \quad (11.41)$$

where b is equal to four times the volume of the total number of molecules present.

To find the effect of a finite time of collision due to the attractive forces between the molecules, let the average time of collision of two molecules be τ. Then the time spent in mutual encounter is time lost in bombarding the walls of the container. Hence the effective gas pressure is reduced in the ratio

$$p = \frac{M V^2}{3(v - b)} \cdot \frac{1}{1 + n\tau},$$

where n is the number of molecular collisions per second. Hence, by substituting for n from (11.22),

$$p(1 + \pi s^2 c \nu \tau) = \tfrac{1}{3}\frac{M V^2}{(v - b)};$$

and if we multiply out the L.H.S., substitute the approximate relation $p = \tfrac{1}{3}\rho V^2$ in the small second term, and put V for c, we find

$$p + \tfrac{1}{3}\rho V^3 \pi s^2 \nu \tau = \tfrac{1}{3}\frac{M V^2}{(v - b)}. \quad . \quad . \quad . \quad (11.42)$$

Also, since $\nu = \rho/m$, and $\frac{1}{3}V^3\pi s^2\tau/m$ is constant, say equal to a', for a given gas and temperature, (11.42) gives

$$(p + a'\rho^2)(v - b) = \tfrac{1}{3}MV^2,$$

or

$$\left(p + \frac{a}{v^2}\right)(v - b) = R\theta, \qquad \ldots \ldots (11.43)$$

where $a'\rho^2 = a/v^2$, where a is constant and $R\theta$ is proportional to the kinetic energy of the molecules.

EXERCISES

1. Deduce the Gas Equation from the kinetic theory of gases, explaining clearly the assumptions made in your deduction.

2. Explain the physical significance of the gas constant R on the kinetic theory of gases.

If the density of a gas at N.T.P. (temperature 0° C., pressure 760 mm. of mercury) is 9×10^{-4} gm./c.c., find the root mean square velocity of the gas molecules under these conditions. [$5 \cdot 8 \times 10^4$ cm./sec.]

3. Deduce an expression for the ratio of the specific heats of a monatomic gas at constant pressure and constant volume on the basis of the kinetic theory. What is the effect on the ratio of increasing the atomicity of the molecule?

4. Define *mean free path of a gas molecule* and *molecular diameter*.
Deduce Clausius' relationship connecting these quantities and find the effective diameter of a hydrogen molecule given that Avogadro's number is $6 \cdot 06 \times 10^{23}$ mols./gram. mol. and the mean free path of a hydrogen molecule at N.T.P. is 2×10^{-5} cm. [$2 \cdot 43 \times 10^{-8}$ cm.]

5. How are viscosity and thermal conductivity explained on the kinetic theory of gases?

Deduce an expression for the coefficient of viscosity in terms of the density of a gas and the mean free path and mean velocity of the gas molecules.

6. Deduce an expression for the thermal conductivity of a gas on the kinetic theory of gases and show that the thermal conductivity, the coefficient of viscosity and the specific heat of a gas at constant volume are very closely connected.

7. Enumerate methods for determining Loschmidt's number and describe in detail one method with which you are familiar.

8. What is meant by Brownian movement? Describe an experiment by which Avogadro's number may be deduced from observations on sedimentation equilibrium.

9. Write a short essay on Brownian Motion.

10. Explain how the kinetic theory may be made to take account of the actual (as opposed to the ideal) properties of gases, illustrating your answer by deducing Van der Waals' equation from the kinetic theory.

CHAPTER XII

Isothermal and Adiabatic Expansions

1. Introduction.

A change is said to take place **isothermally** if the temperature remains constant throughout the change. An **adiabatic** change is defined as one in which heat energy is neither gained nor lost by the system. In gas phenomena changes generally take place in practice under some intermediate condition where the temperature is not constant and where heat is transferred either to or from the surroundings.

2. Work Done by a Gas on Expansion.

We first consider the special conditions shown in fig. 1, where the gas is contained in a cylinder fitted with a piston of area of cross-
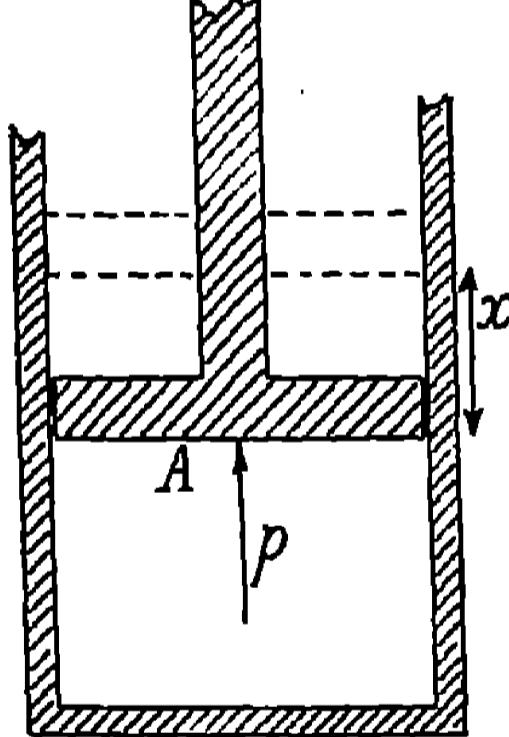
Fig. 1.—Work done by a
Gas on Expansion
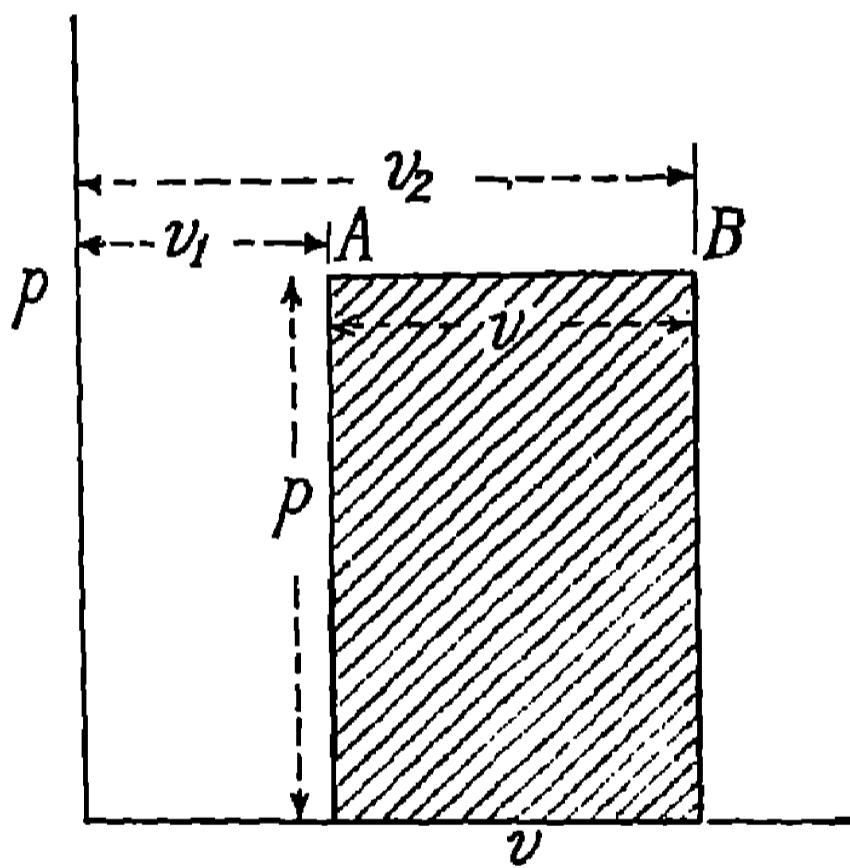
Fig. 2.—Work done at Constant
Pressure

section A. Suppose the pressure p of the gas is kept constant and the gas is allowed to expand, thereby moving the piston through a distance x. Then

$$\text{work done} = \text{force} \times \text{distance} = pA \cdot x = pv, \quad . \quad (12.1)$$

where v is the increase in volume of the gas.

We can represent the expansion graphically by the horizontal line AB in fig. 2, where the increase in volume v is $(v_2 - v_1)$. Now the

area between AB and the volume axis is pv: hence the *work done is represented by the area between the (p-v) curve and the volume axis.*

This statement holds also when the pressure does not remain constant on expansion, the work done in fig. 3 being equal to the area ABCD or, in the notation of the integral calculus, $\int p \, dv$, where integration extends over the limits of the volume change.
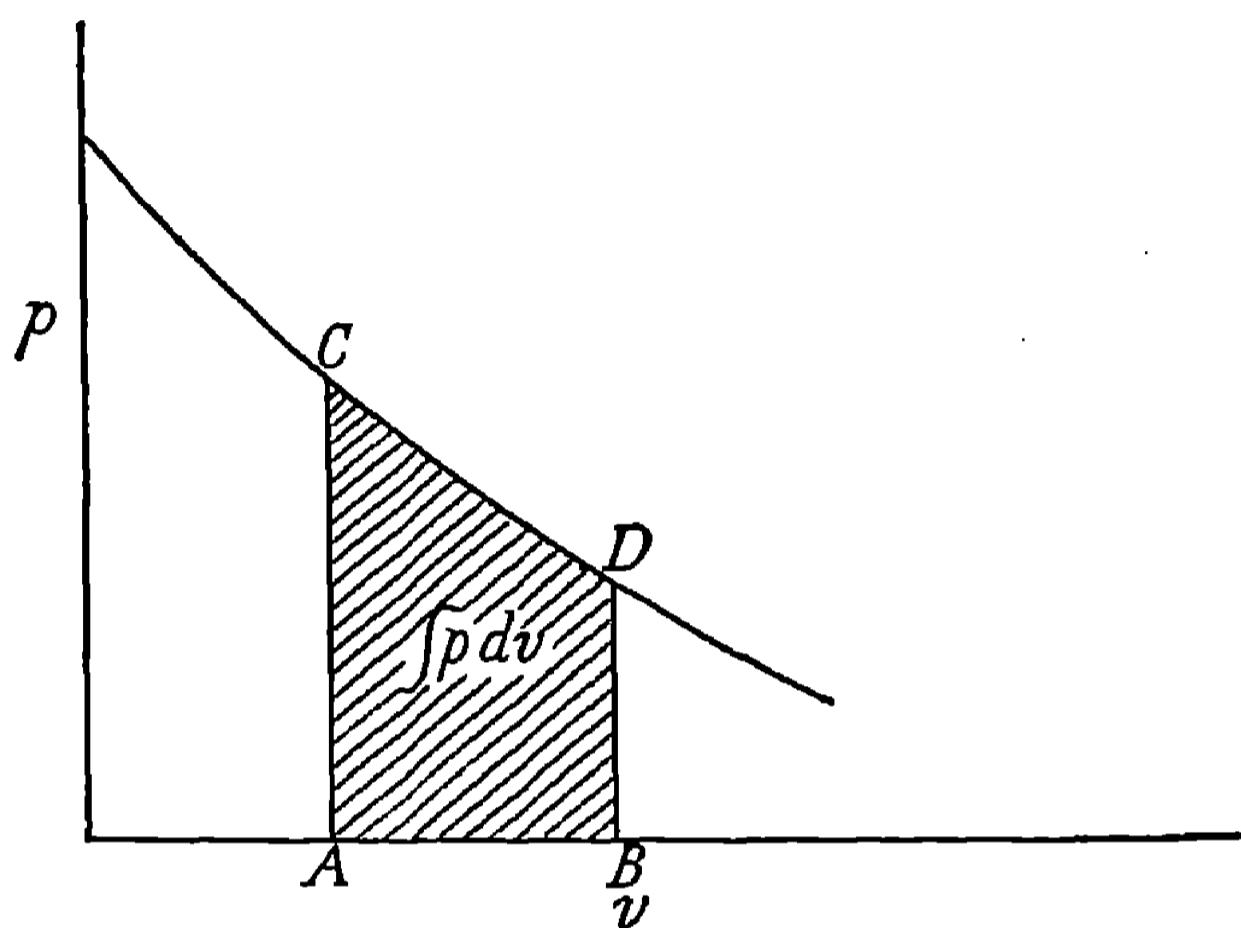
Fig. 3.—Work done represented by an Area

3. Specific Heats of Gases and External Work.

It follows from the First Law of Thermodynamics (Chap. VI) that heat absorbed by a body is equivalent to the external work done + the increase of internal energy.

Now, for gases, Joule proved experimentally that the internal energy approximately depends on the temperature only; and for a perfect gas the property is assumed to hold exactly. Consider, then, two changes in the state (p, v, θ) of a gram-molecule of a perfect gas, the one change at constant pressure, the other at constant volume, and the change of temperature $d\theta$ the same in both cases. If J is Joule's equivalent, we have

$$C_p d\theta - \frac{p \, dv}{J} = C_v d\theta, \quad \ldots \quad (12.2)$$

for each side represents the change in internal energy, which depends, as we have just seen, on $d\theta$ only.

Now, from the gas equation,

$$pv = R\theta.$$

Hence, at constant pressure, differentiating to obtain the small increase in volume dv accompanying the small rise in temperature $d\theta$,

$$p\,dv = R\,d\theta. \quad . \quad . \quad . \quad . \quad . \quad (12.3)$$

From (12.2) and (12.3) we derive the important expression

$$C_p = C_v + \frac{R}{J}. \quad . \quad . \quad . \quad . \quad . \quad (12.4)$$

If R is expressed in calories, the equivalent J is, of course, not introduced. Equation (12.4) has been used to determine Joule's equivalent from experiments on C_p, C_v and R. We have also used (12.4) in deducing $\gamma = 5/3$ for an ideal monatomic gas on p. 95.

4. Isothermal Expansions.

Consideration of the thermal properties of substances soon shows that strictly isothermal expansions cannot occur in practice. As soon as a gas expands it does some external work; consequently its temperature falls and the expansion is no longer isothermal. By making the walls of the container of material of very high conductivity, and letting the expansion occur very slowly, an approximation to isothermal conditions occurs when heat energy is supplied through the walls as rapidly as it is used in performing mechanical work by the expanding gas. If a gas expands *isothermally* from volume v_1 to volume v_2, the work done is

$$W = \int_{v_1}^{v_2} p\,dv = k \int_{v_1}^{v_2} \frac{dv}{v}, \quad . \quad . \quad . \quad . \quad (12.5)$$

since for an isothermal change, Boyle's law, that is $pv = k$ (constant), is obeyed. Integrating (12.5), we get

$$W = k \log_e \frac{v_2}{v_1},$$

which, by the gas equation $pv = R\theta$, may be written

$$W = p_1 v_1 \log_e \frac{v_2}{v_1} = p_2 v_2 \log_e \frac{v_2}{v_1} = R\theta \log_e \frac{v_2}{v_1}$$

$$= R\theta \log_e \frac{p_1}{p_2}. \quad . \quad . \quad . \quad . \quad . \quad (12.6)$$

5. Adiabatic Expansions.

For a perfect adiabatic expansion the gas would have to be contained in a perfect heat insulator so that no energy transfer took place to the surroundings. These conditions are realized by allowing the gas to expand rapidly inside a poor conductor. The expansion has

then occurred before any appreciable quantity of heat has leaked through from the surroundings. Since external work is done by the gas when it expands, the loss in energy results in a cooling of the gas. Conversely, a heating occurs during an adiabatic compression.

We proceed to show that the equation between pressure and volume governing adiabatic expansions is

$$pv^\gamma = \text{constant},$$

where γ is the ratio of the specific heats of the gas at constant pressure and constant volume respectively. Suppose a gram-molecule of gas is allowed to undergo a small adiabatic expansion dv; and let the changes of temperature and internal energy be $d\theta$ and du_1. Hence

$$du_1 = -p\,dv. \qquad \ldots \ldots \quad (12.7)$$

If the same change of temperature took place at constant volume, the change of internal energy in that case being du_2, then

$$du_2 = C_v\,d\theta. \qquad \ldots \ldots \quad (12.8)$$

But, from Joule's experimental law just cited, $du_1 = du_2$. Hence

$$p\,dv = -C_v\,d\theta. \qquad \ldots \ldots \quad (12.9)$$

Now, during the adiabatic expansion, pressure, volume and temperature change. Hence, differentiating the gas equation, we have

$$p\,dv + v\,dp = R\,d\theta. \qquad \ldots \ldots \quad (12.10)$$

Since we require a relation between p and v, we eliminate θ between (12.9) and (12.10), and obtain

$$p\,dv = -C_v\frac{(p\,dv + v\,dp)}{R}. \qquad \ldots \ldots \quad (12.11)$$

From (12.4), if R is in heat units, $R = C_p - C_v$. Hence (12.11) becomes

$$p\,dv = -C_v\frac{(p\,dv + v\,dp)}{C_p - C_v},$$

which gives

$$C_p p\,dv = -C_v v\,dp,$$

or

$$\gamma\frac{dv}{v} = -\frac{dp}{p}, \qquad \ldots \ldots \quad (12.12)$$

where $\gamma = C_p/C_v$. Integrating (12.12), we obtain

$$\gamma \log_e v = -\log_e p + \text{constant},$$

or

$$\log_e pv^\gamma = \text{constant},$$

whence

$$pv^\gamma = \text{constant}. \qquad \ldots \ldots \quad (12.13)$$

Proceeding as in the previous section, we may find the work done by a gas in an adiabatic expansion, remembering that $pv^\gamma = k$, instead of $pv = k$ when Boyle's law is obeyed and the expansion is isothermal. Equation (12.5) therefore becomes in the adiabatic case,

$$W = \int_{v_1}^{v_2} p\,dv = k\int_{v_1}^{v_2} \frac{dv}{v^\gamma} = \left[\frac{kv^{1-\gamma}}{1-\gamma}\right]_{v_1}^{v_2} \quad . \quad . \quad (12.14)$$

Since
$$p_1v_1^\gamma = p_2v_2^\gamma = k,$$
$$p_1v_1 = R\theta_1,$$
and
$$p_2v_2 = R\theta_2,$$

equation (12.14) may be written in a variety of forms, thus:

$$W = \frac{p_1v_1^\gamma}{(\gamma-1)}\left(\frac{1}{v_1^{\gamma-1}} - \frac{1}{v_2^{\gamma-1}}\right) = \frac{1}{(\gamma-1)}\left(\frac{p_1v_1^\gamma}{v_1^{\gamma-1}} - \frac{p_2v_2^\gamma}{v_2^{\gamma-1}}\right)$$

$$= \frac{(p_1v_1 - p_2v_2)}{\gamma-1}, \quad . \quad . \quad . \quad . \quad (12.15)$$

or
$$W = \frac{R}{(\gamma-1)}(\theta_1 - \theta_2). \quad . \quad . \quad . \quad (12.16)$$

6. Clement and Désormes' Experiment.

Since the equation $pv^\gamma = $ const. governs adiabatic changes, the student will realize that the exact knowledge of the ratio of the specific heats is quite as important as the knowledge of the individual values of c_p and c_v. The ratio γ is obtained directly from the velocity of sound in the gas, as described in Part IV; it can now be calculated more accurately from the theory of band spectra than it can be measured by direct experiment.

Fig. 4.—Clement and Désormes' Experiment

An interesting experimental determination, now only of historical and laboratory interest, is the determination of γ by Clement and Désormes' apparatus. As shown in fig. 4, a large container is fitted with a manometer containing some liquid of low density such as paraffin. Pressures differing little from atmospheric pressure may thus be easily read. The container is surrounded by cotton wool and fitted with an inlet valve through which air may be forced by a pump. A large outlet valve at the top of the container allows the air to expand
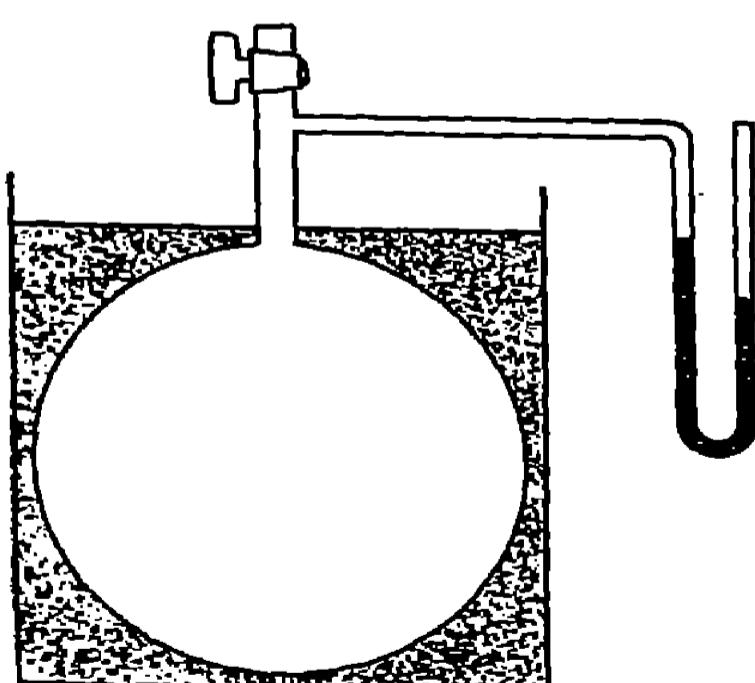
sufficiently suddenly for the expansion to be approximately adiabatic. A pressure slightly above atmospheric, as indicated by a difference h_1 in the arms of the manometer, is first established. The gas is then expanded adiabatically by opening the outlet valve just sufficiently long to allow the pressure to fall to atmospheric. The valve is then closed. On allowing the apparatus to stand for five or ten minutes, the pressure rises to some new steady value h_2. This is because the gas in the container cools on the adiabatic expansion and finally regains room temperature with consequent rise of pressure. We proceed to show that approximately

$$\gamma = \frac{h_1}{h_1 - h_2}. \qquad \qquad (12.17)$$

Referring to fig. 5, let $p_3 v_3$ be the final pressure and volume in the container. The gas which now occupies v_3, initially occupied a smaller
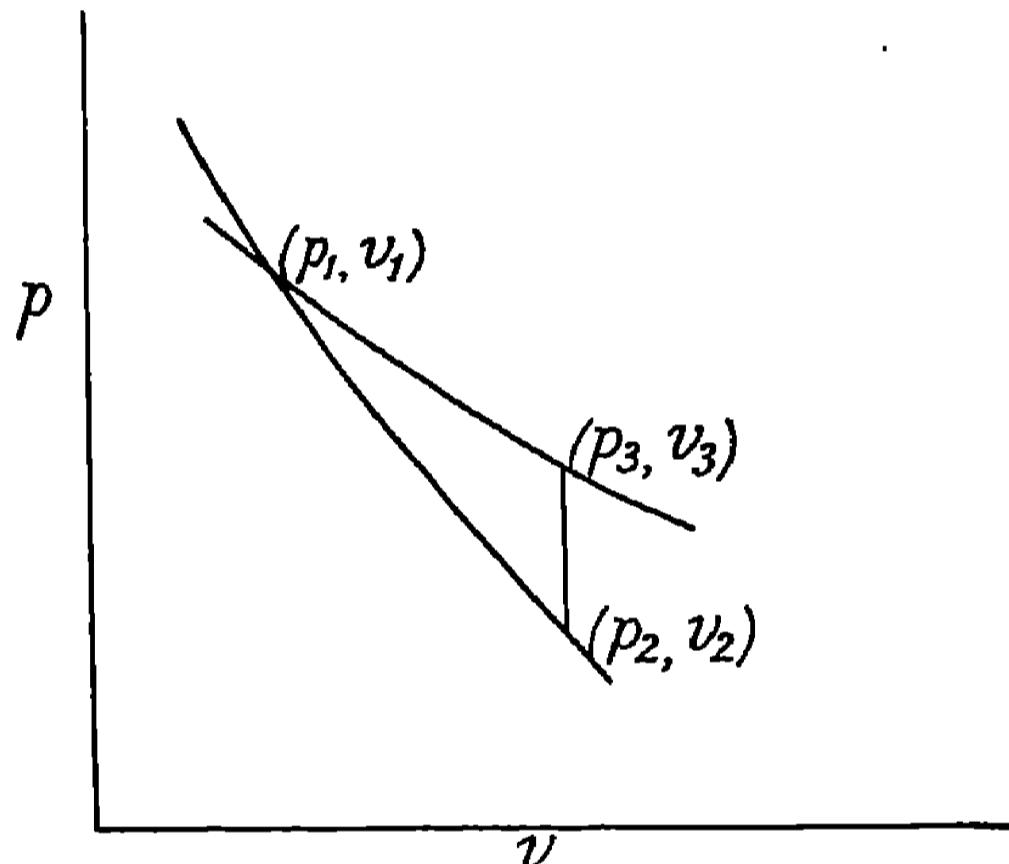
Fig. 5.—Adiabatic and Isothermal Curves

volume v_1 at the initial pressure p_1. On expanding adiabatically the pressure fell to p_2 (atmospheric) and the volume increased to v_2. When the gas had regained room temperature, the pressure rose to p_3 and the volume increased to v_3. Since the increase to volume v_3 from v_2 is only due to the rise in the level of the manometer, and is negligible compared with the volume of the container, v_3 is almost equal to v_2, and is put equal to it in the following calculation. For the adiabatic expansion

$$p_1 v_1{}^\gamma = p_2 v_2{}^\gamma = p_2 v_3{}^\gamma. \qquad \dots \quad (12.18)$$

In the initial and final state the gas is at the same (room) temperature. Hence these two states are connected isothermally and consequently

$$p_1 v_1 = p_3 v_3 \qquad \dots \dots \quad (12.19)$$

by Boyle's law.

Eliminating v_1 and v_3 from (12.18) and (12.19), we get

$$\left(\frac{p_1}{p_2}\right) = \left(\frac{p_1}{p_3}\right)^\gamma,$$

or

$$\gamma = \frac{\log p_1 - \log p_2}{\log p_1 - \log p_3}$$

$$= \frac{p_1 - p_2}{p_1 - p_3} \qquad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (12.20)$$

approximately, since p_1, p_2 and p_3 are not very different from each other.

But $\qquad\qquad p_1 = p_2 + h_1$ and $p_3 = p_2 + h_2$;

hence $\qquad\qquad\qquad \gamma = \frac{h_1}{h_1 - h_2}.$

7. Expansion of Gases in Practice.

Since in general an expansion is neither purely isothermal nor purely adiabatic, the equation governing pressure and volume changes
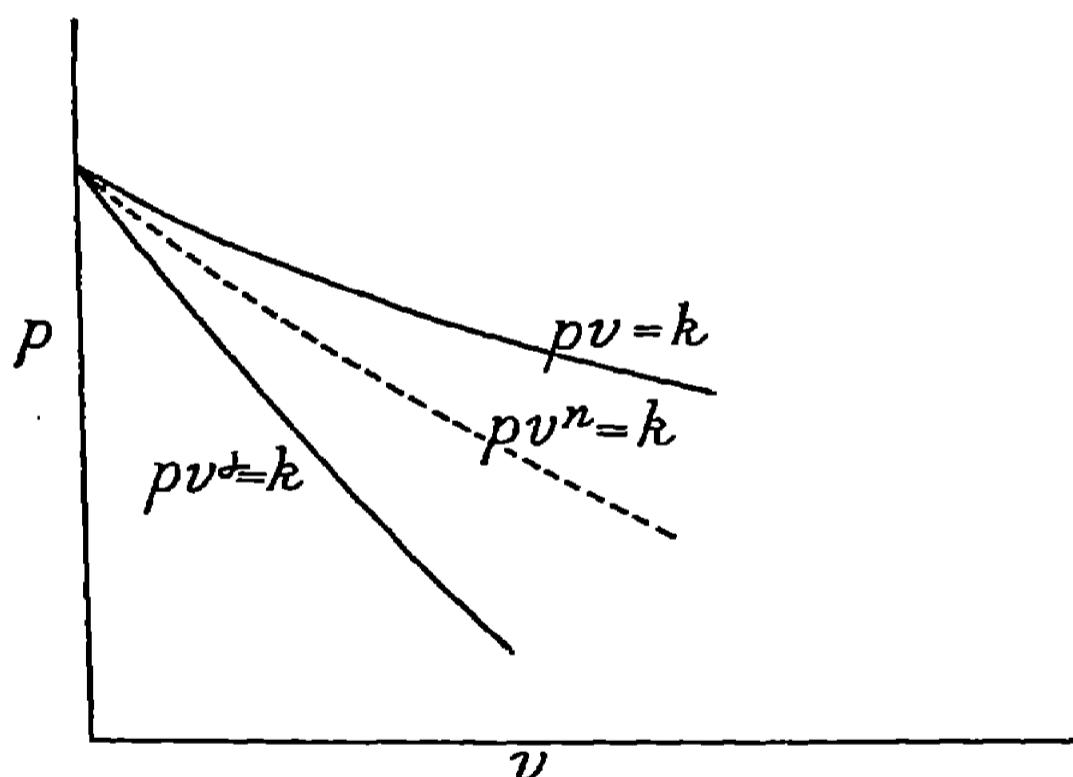
Fig. 6.—Adiabatic, Isothermal and Intermediate Curves

may be taken to be $pv^n = $ const., where n lies between γ and unity. We represent the three types of expansion and compression in fig. 6. The curve governing the adiabatic change is always steeper than the corresponding isothermal, the intermediate type of change being shown by the dotted curve.

EXERCISES

1. Show that the work done when a gas expands is given by the area enclosed between the p-v curve and the v-axis. What are indicator diagrams?

2. Distinguish between *isothermal* and *adiabatic* expansions.
Obtain an expression for the relation between pressure and volume of a gas during an adiabatic change.

3. A gram-molecule of xenon at 15° C. is suddenly expanded to 10 times its original volume. Find the final temperature momentarily attained. [−212° C.]

4. Describe an experiment by which the ratio of the specific heat of a gas at constant pressure to its specific heat at constant volume may be obtained directly.
Why may a gas be considered to possess a variable specific heat between certain limiting values?

5. Obtain an expression for the work done when a gas undergoes isothermal expansion, and find the work done when a gram-molecule of gas at 183° C. expands isothermally until its volume is doubled. [628 cal.]

6. Give practical examples of gases undergoing adiabatic changes.
What is the work done when a gram-molecule of helium at 0° C. is suddenly compressed to a pressure twenty times its initial value? [1883 cal.]

CHAPTER XIII

* Elementary Thermodynamics

1. Carnot's Cycle.

If a gas is submitted to a series of changes of pressure and volume and is ultimately brought back to its initial conditions, it is said to undergo a cycle of operations. A cycle of particular importance is that examined by Carnot and represented in fig. 1. Imagine a gas with initial pressure p_1 and volume v_1, represented by the point A. Let the
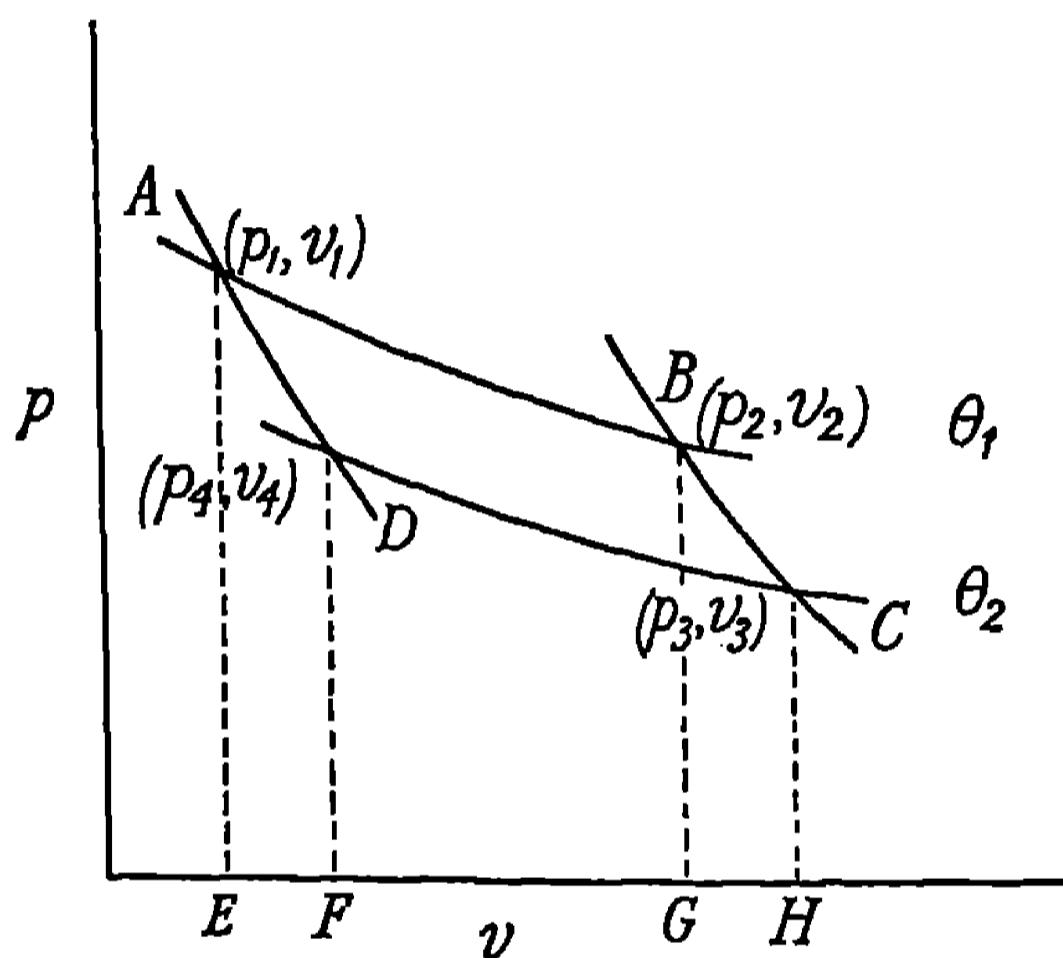
Fig. 1.—Carnot's Cycle

gas expand isothermally down the isothermal at θ_1 until it reaches condition B, when its pressure and volume are p_2, v_2. Let the expansion now proceed adiabatically down the adiabatic BC to C, where the pressure and volume are p_3 and v_3. Now compress the gas isothermally along the isothermal CD at temperature θ_2 until it reaches D (on the adiabatic through A), where p_4 and v_4 represent its pressure and volume. Finally, compress the gas adiabatically from D to A until it regains its initial pressure and volume (p_1, v_1).

The net amount of work done by the gas in the cycle will be the difference between the work done by the gas in expanding from A to B, and B to C, and the work done in compressing the gas from C to D, and D to A. Now by our statement in Chap. XII, section 2, the work done is represented by the area between the $(p\text{-}v)$ curve and the

v-axis. The net work done is therefore the difference in the areas (ABGE + BCHG) — (CDFH + DAEF), which is the area ABCD. In Carnot's cycle, therefore, *the net work done is equal to the area enclosed between the adiabatic and the isothermal curves.*

2. Reversible Cycles.

We could clearly have traversed the cycle in the preceding section in the reverse direction ADCBA, when we should have arrived at the same conclusions. Carnot's cycle is therefore strictly reversible. If we examine the cycle in more detail, we see that such a cycle cannot be exactly traversed by any real substance because (*a*) purely isothermal and adiabatic changes are not possible owing to the imperfect heat conduction and insulation of the container, (*b*) there is always a certain amount of heat lost irreversibly in any real cycle.

An example of irreversible heat loss is the heat generated by friction when a piston moves in a cylinder. When the gas expands and pushes the piston out, a certain amount of mechanical energy is provided plus a certain amount of frictional heat produced. Now for a strictly reversible movement of the piston, when the gas is compressed to its original state, frictional heat should be absorbed. This never occurs in practice, where friction always evolves heat.

3. Heat Engines.

The apparatus implied in traversing the cycle ABCD is said to be a *heat engine*. During the change from A to B, heat is taken in from some source maintained at θ_1. This supply is cut off at B, and the gas expands doing external work under its own energy down the adiabatic BC. Consequently its temperature falls; at C the compression stroke is commenced, and heat is removed during the compression so that the latter takes place isothermally at θ_2 from C to D. Finally, the compression is completed adiabatically, so that the temperature rises to θ_1 when we return to A.

4. Efficiency of a Reversible Cycle.

We define the efficiency of a cycle as

$$E = \frac{\text{net mechanical work done in the cycle}}{\text{heat taken in at the higher temperature}}. \quad . \quad (13.1)$$

Since the net work done is the area ABCD, if H_1 and H_2 are the heats taken in and given out along AB and CD respectively,

$$E = \frac{\text{ABCD}}{H_1} = \frac{H_1 - H_2}{H_1}. \quad . \quad . \quad . \quad (13.2)$$

Equation (13.2) states that the net mechanical energy available is the difference between H_1, the heat absorbed by the engine from the source at θ_1, and H_2, the heat given up to the condenser at θ_2. This is simply an application of the principle of conservation of energy, for the initial and final states of the gas are the same, so that there is no change in the internal energy.

From equation (12.6),

$$H_1 = R\theta_1 \log_e \frac{p_1}{p_2}, \qquad \qquad (13.3)$$

and

$$H_2 = R\theta_2 \log_e \frac{p_4}{p_3}.$$

Hence, from (13.2) and (13.3),

$$E = \frac{\theta_1 \log_e \frac{p_1}{p_2} - \theta_2 \log_e \frac{p_4}{p_3}}{\theta_1 \log_e \frac{p_1}{p_2}}. \qquad (13.4)$$

Now, since A and D, B and C lie on adiabatics,

$$p_1 v_1{}^\gamma = p_4 v_4{}^\gamma, \qquad \qquad (13.5)$$

and

$$p_2 v_2{}^\gamma = p_3 v_3{}^\gamma.$$

Also, since A and B, C and D lie on isothermals,

$$p_1 v_1 = p_2 v_2, \qquad \qquad (13.6)$$

and

$$p_3 v_3 = p_4 v_4.$$

Hence, from (13.5) and (13.6),

$$p_1/p_2 = p_4/p_3, \qquad \qquad (13.7)$$

so (13.2), (13.4) and (13.1) become

$$E = \frac{H_1 - H_2}{H_1} = \frac{\theta_1 - \theta_2}{\theta_1} = \frac{\text{external work done}}{\text{heat taken in at higher temperature}}.$$

$$(13.8)$$

Equation (13.8) is of great importance, and we shall use it to deduce many physical results in later sections of this chapter.

5. Second Law of Thermodynamics.

If we have a large mass of a given substance at a temperature slightly lower than that of a small mass of the same substance, although the total energy contained in the former is much greater than that contained in the latter, it is quite impossible experimentally to liberate this energy by using the former as source and the latter as

condenser in a heat engine. The flow of heat is governed entirely by the temperature. This fact is one way of putting the **Second Law of Thermodynamics**, which states that *no self-acting machine will operate using a body of lower temperature as source and giving up heat to a body at higher temperature.*

From this law we can show that the efficiency of all reversible heat engines is the same. Consider two reversible heat engines A and B, working between the same temperatures; it is sufficient if we show that E_B cannot be greater than E_A. Let B drive A backwards; and let B absorb heat H_{1B} at the higher temperature θ_1 and give out heat H_{2B} at θ_2. Then

$$E_B = \frac{H_{1B} - H_{2B}}{H_{1B}}.$$

Similarly, let the heat given out by A at the high temperature be H_{1A}, and that absorbed at the lower temperature be H_{2A}. Then

$$E_A = \frac{H_{1A} - H_{2A}}{H_{1A}}.$$

If it were possible that $E_B > E_A$, then

$$\frac{H_{1B} - H_{2B}}{H_{1B}} > \frac{H_{1A} - H_{2A}}{H_{1A}}. \quad \cdots \quad (13.9)$$

Now the work done by B is done on A: hence

$$H_{1B} - H_{2B} = H_{1A} - H_{2A}. \quad \cdots \quad (13.10)$$

Hence, from (13.9),

$$H_{1A} > H_{1B}, \quad \cdots \cdots \quad (13.11)$$

and consequently, by substituting from (13.11) in (13.10),

$$H_{2A} > H_{2B}. \quad \cdots \cdots \quad (13.12)$$

Now, if (13.11) and (13.12) were true, a net amount of heat would be extracted from the condenser at θ_2 and given to the source at the higher temperature θ_1. This is contrary to the second law of thermodynamics; consequently E_B must equal E_A.

This result, that the efficiencies of all perfectly reversible engines are the same, is one aspect of a very important part of thermodynamics; for it implies that, provided a cycle is reversible, its *behaviour is independent of the nature of the working substance.* Hitherto, we have only considered perfect gases as working substances; in later sections we propose to extend the applications of thermodynamics to such diverse physical phenomena as surface tension and thermo-electricity.

6. Absolute or Work Scale of Temperature.

Consider two adiabatics ACE, BDF, crossed at regular intervals by isothermals AB, CD, EF, as in fig. 2. Suppose the work done in the cycles ABDC, CDFE, &c., is the same: then we may introduce a new temperature scale *defining* the temperature intervals $(T_1 - T_2)$, $(T_2 - T_3)$ to be equal if equal work is done in the cycles ABDC, CDFE, &c. Such a scale is termed an *absolute* or *work scale of temperature*. As we proceed to lower and lower temperatures we may ultimately arrive at a temperature where no heat remains to be given to the condenser, all the heat taken in at the higher temperature being con-
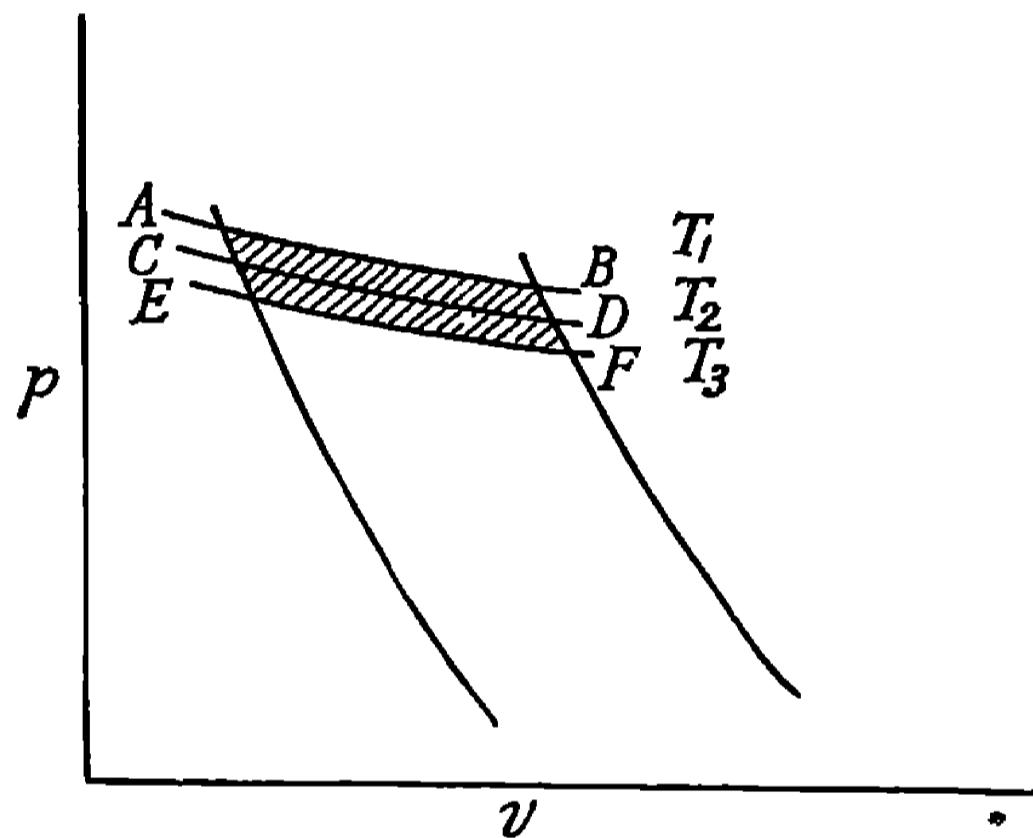
Fig. 2.—Absolute Scale of Temperature

verted into mechanical work. Such a temperature would constitute a natural *absolute zero*.

The efficiency of all the reversible cycles such as ABDC, CDFE is the same, and is defined by (13.1), where

$$E = \frac{H_1 - H_2}{H_1} = \frac{(T_1 - T_2)}{a}, \quad . \quad . \quad . \quad (13.13)$$

where T_1 and T_2 are temperatures on the absolute scale and a is some function of T_1. Now for the last cycle above absolute zero, all the heat is converted into mechanical work. We therefore have $E = 1$; also $T_2 = 0$, so equation (13.13) gives $a = T_1$. Hence, the efficiency equation becomes

$$E = \frac{H_1 - H_2}{H_1} = \frac{T_1 - T_2}{T_1}, \quad . \quad . \quad . \quad (13.14)$$

which is identical with (13.8), thus showing that **the absolute scale coincides with the perfect gas scale.**

7. Effect of Pressure on the Freezing-point of a Liquid.

In fig. 3, let ABCD be one complete isothermal covering the change of state at temperature $(\theta + d\theta)$ and EFGH the corresponding isothermal at temperature θ. Then if we draw adiabatics through B and C, we may regard the path BCPQ as a heat cycle. If we work with unit mass of material, the heat taken in along BC is $H_1 = L$, where L is the latent heat of fusion. Again, the work done in the cycle is the area BCPQ, which is approximately equal to $dp \cdot (v_2 - v_1)$, where
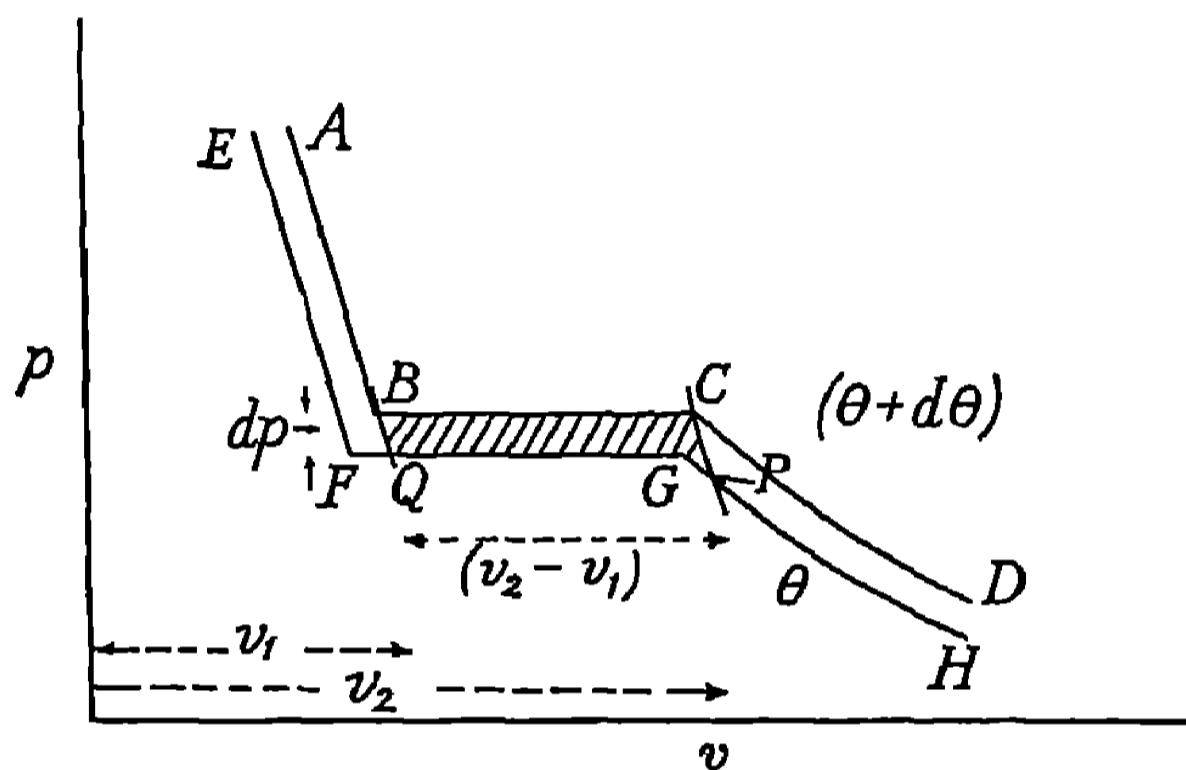
Fig. 3.—Effect of Pressure on the Freezing-point

$(v_2 - v_1)$ is the change in volume which occurs when unit mass of the material changes from liquid to solid at a pressure p. Hence, applying (13.8),

$$E = \frac{(\theta + d\theta) - \theta}{\theta} = \frac{dp(v_2 - v_1)}{L},$$

or

$$d\theta = \frac{dp(v_2 - v_1)}{L} \theta, \qquad . \ . \ . \ . \ . \ . \ . \quad (13.15)$$

an equation which gives the elevation $d\theta$ in freezing-point consequent upon a rise dp in pressure. Since $v_2 < v_1$ for water and ice, $d\theta$ comes out negative when dp is positive, as is observed.

8. Temperature Dependence of the Osmotic Pressure of a Dilute Solution.

We mentioned in Part I, p. 127, that the mechanism of osmotic pressure is still not well understood. Since, however, the application of thermodynamics is not concerned with the mechanism involved, provided we can construct a reversible cycle we may apply the principles of thermodynamics to deduce some of the laws of osmosis. We

consider a quantity of dilute solution enclosed in a cylindrical vessel as shown in fig. 4, fitted with a frictionless piston, the top of which is semi-permeable, allowing pure solvent only to pass through it. Let the volume of the solution be V, its osmotic pressure P, and its absolute temperature θ. As the piston moves, pure solvent may pass through the piston-head into the region above or vice versa. The system is now taken round the reversible cycle LMNO of fig. 5. The point L represents the condition (P_1, V_1, θ), when the piston is at AB. The piston then moves slowly upwards admitting a volume dV of solvent through the piston; the system therefore moves to the point M of fig. 5, the operation having been carried out at constant
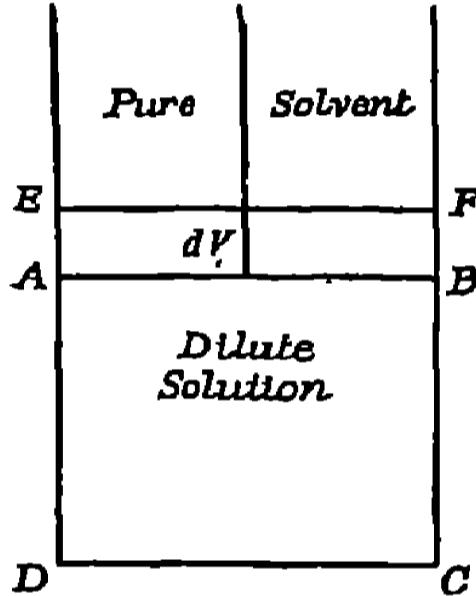
Fig. 4.—Osmotic Pressure
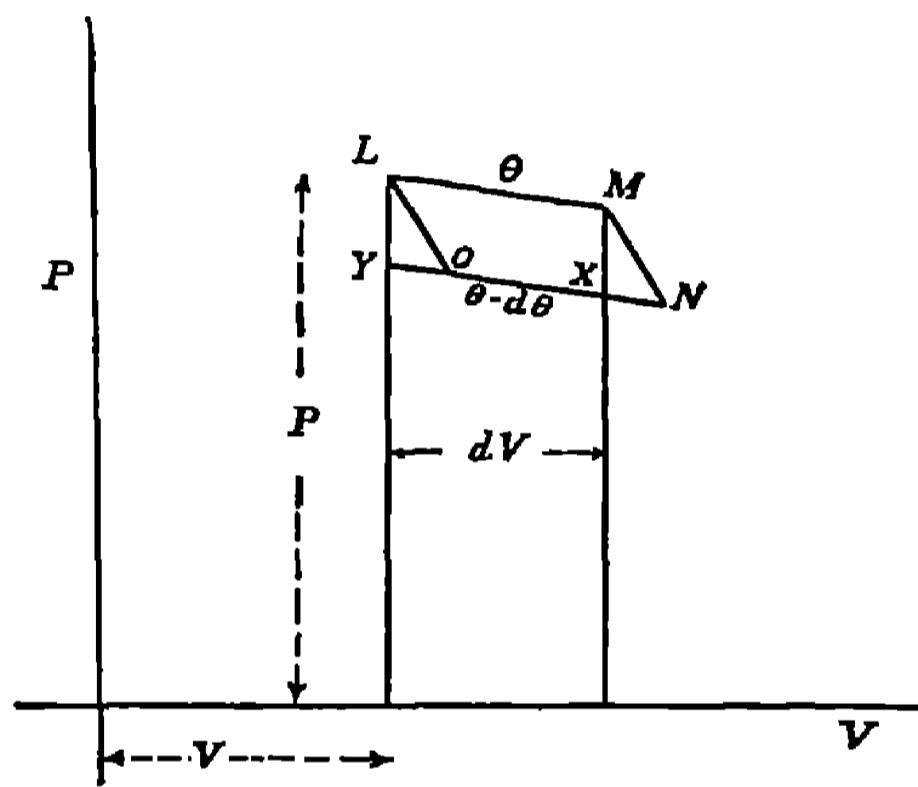
Fig. 5.—Carnot Cycle

temperature. Continue the cycle to N, allowing the solvent to pass through adiabatically from M to N; this is accompanied by a drop in temperature $d\theta$. Next depress the piston until the conditions are represented by O; this compression takes place isothermally along NO. Finally, complete the cycle by a small adiabatic compression represented by the path OL.

Applying the efficiency equation (13.8),

$$\frac{d\theta}{\theta} = \frac{dP \cdot dv}{P \cdot dv},$$

or

$$\int \frac{d\theta}{\theta} = \int \frac{dp}{P},$$

whence by integration

$$\log P = \log \theta + \text{constant},$$

or

$$P = a\theta,$$

where a is a constant. We have therefore deduced from thermodynamics the experimental law stated in Part I, p. 127, that the osmotic pressure of a dilute solution is proportional to the absolute temperature.

9. Surface Tension and Surface Energy.

To examine the relation between surface tension and surface energy (see Part I, p. 116), consider a heat engine consisting of a rectangular soap-film as in fig. 6. Suppose, as actually occurs, when the film is stretched it absorbs heat from the surroundings, whereas. when the film contracts this heat is evolved reversibly. Let the film now be taken round a cycle in which:

(1) It is increased by area A, isothermally at temperature θ, when its surface tension is S. Assume the heat absorbed reversibly is h per unit area. The work done by the film is $(-SA)$.

Fig. 6.—Surface Tension and Surface Energy

(2) Now place the film in an enclosure at temperature $\theta + \delta\theta$, keeping the area constant. The surface tension changes to $\left(S + \dfrac{dS}{d\theta}\delta\theta\right)$.

(3) Now let the film return isothermally to its original area. The work done on the film is $(-)\left(S + \dfrac{dS}{d\theta}\delta\theta\right)A$.

(4) Finally, replace the film in the enclosure at θ so that it returns to its original condition.

Applying the efficiency equation, we have

$$E = \frac{\theta - (\theta + \delta\theta)}{\theta} = \frac{-SA + \left(S + \dfrac{dS}{d\theta}\delta\theta\right)A}{hA},$$

or

$$h = -\theta \frac{dS}{d\theta}. \qquad \qquad (13.16)$$

10. Action of Reversible Primary Cells.

In Part V we shall see that a certain amount of chemical action in a cell corresponds to a certain amount of electrical energy liberated. It was therefore suggested, on the basis of the conservation of energy, that the excess of chemical energy was exactly equal to the electrical energy liberated. We proceed to show that this relation requires

9

correction if any heat is absorbed or evolved reversibly during the operation of the cell.

Let h be the heat absorbed thermodynamically for passage of unit quantity of electricity through the cell, and let H be the corresponding heat formed in the chemical reaction and V the electrical energy liberated. Then

$$V = H + h. \qquad \ldots \ldots \quad (13.17)$$

Proceeding as in the preceding sections, let a quantity of electricity q be passed by the cell in an isothermal enclosure at θ when the E.M.F. of the cell is E. Then the work done by the cell is Eq. At the same time a quantity of heat hq is absorbed thermodynamically. Now place the cell in an isothermal enclosure at $\theta - \delta\theta$, when its E.M.F. changes to $\left(E - \dfrac{dE}{d\theta}\delta\theta\right)$, and pass a quantity of electricity q through the cell. The work done on the cell is $\left(E - \dfrac{dE}{d\theta}\delta\theta\right)q$. Hence, if the cell is finally allowed to return to its original temperature θ, the efficiency equation gives

$$\frac{\delta\theta}{\theta} = \frac{dE}{d\theta}\delta\theta\frac{q}{hq},$$

or

$$h = \theta\frac{dE}{d\theta}.$$

Hence equation (13.17) becomes

$$V = H + \theta\frac{dE}{d\theta}, \qquad . \quad . \ . \ . \quad (13.18)$$

or, since $V = E$,

$$E = H + \theta\frac{dE}{d\theta}.$$

The simple relation between chemical energy and electrical energy $V = H$ holds therefore only if $dE/d\theta$ is zero, that is, the cell has zero coefficient of change of E.M.F. with temperature. This happens to be approximately true for the Daniell cell, and hence the treatment given in Part V is approximately correct.

11. Entropy.

If we subtract unity from each side of the efficiency equation (13.8), we obtain

$$\frac{H_2}{H_1} = \frac{\theta_2}{\theta_1},$$

or, if H stands for heat *absorbed*, so that heat given out is negative,

$$\Sigma\frac{H}{\theta} = \text{zero}, \qquad . \ . \ . \ . \ . \ . \quad (13.19)$$

in a reversible cycle. The expression $\Sigma\dfrac{H}{\theta}$ or $\displaystyle\int_{\theta_1}^{\theta_2}\dfrac{dH}{\theta}$ is said to represent the *change in entropy* of a system. For real systems, which are not exactly reversible, the change in entropy is always positive. Entropy defined as above is a mathematical rather than a physical conception. It allows the Second Law of Thermodynamics to be stated in the form that the entropy of a real system always increases. On examination this statement is found to imply (cf. section 5) that although the total amount of energy in a system remains constant, that energy becomes so distributed as time proceeds that it becomes less and less able to do work. In fact, a dead level of temperature is eventually attained. It is in this sense that the Universe is said to be " running down ".
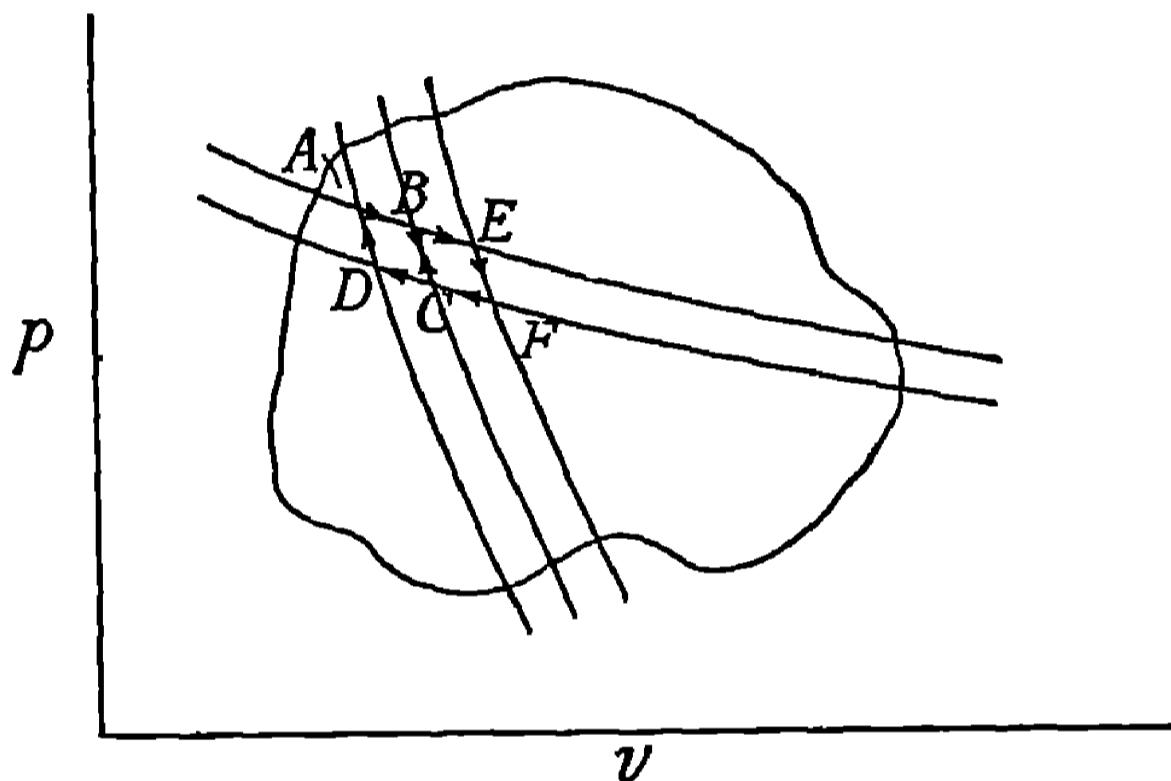
Fig. 7.—Entropy Equation for any Cycle

If we have a cycle with the outline shown in fig. 7, then provided the cycle is reversible it still obeys the entropy equation $\Sigma\dfrac{H}{\theta}=0$. We can see this by dividing the area into a large number of small Carnot cycles by drawing adiabatics and isothermals. Then in traversing each infinitesimal Carnot cycle part of the work done *on* the gas in one cycle exactly neutralizes part of the work done *by* the gas in the adjacent cycle. Thus, in fig. 7, the side BC is common to the cycles ABCDA, BEFCB, but it is oppositely traversed. When all the infinitesimal cycles are considered, this mutual cancelling occurs for all interior sides. Hence, in the limit, the net work done is that done in describing the circumference of the area.

12. Effect of Pressure on the Boiling-point of a Liquid.

Consider the transition from liquid to vapour for two isothermals at θ and $(\theta + d\theta)$ as shown in fig. 8. Then considering the reversible

cycle ABCD, if s_1 is the specific heat of the fluid while traversing BC, and s_2 its specific heat while traversing DA, the First Law of Thermodynamics applied to unit mass of the substance gives

$$\left(L + \frac{dL}{d\theta}\delta\theta\right) - L + s_2\delta\theta - s_1\delta\theta = \text{work done in cycle}$$

$$= \text{ABCD} = \delta p(v_1 - v_2),$$

where $\qquad L = \text{latent heat of vaporization at } \theta,$

$$\left(L + \frac{dL}{d\theta}\delta\theta\right) = \text{latent heat of vaporization at } (\theta + \delta\theta),$$

$$\delta p = \text{pressure change},$$

$v_1, v_2 = $ volume of unit mass of vapour and liquid respectively at pressure p.

Hence $\qquad \dfrac{dL}{d\theta} + (s_2 - s_1) = (v_1 - v_2)\dfrac{dp}{d\theta}.$ . . . (13.20)
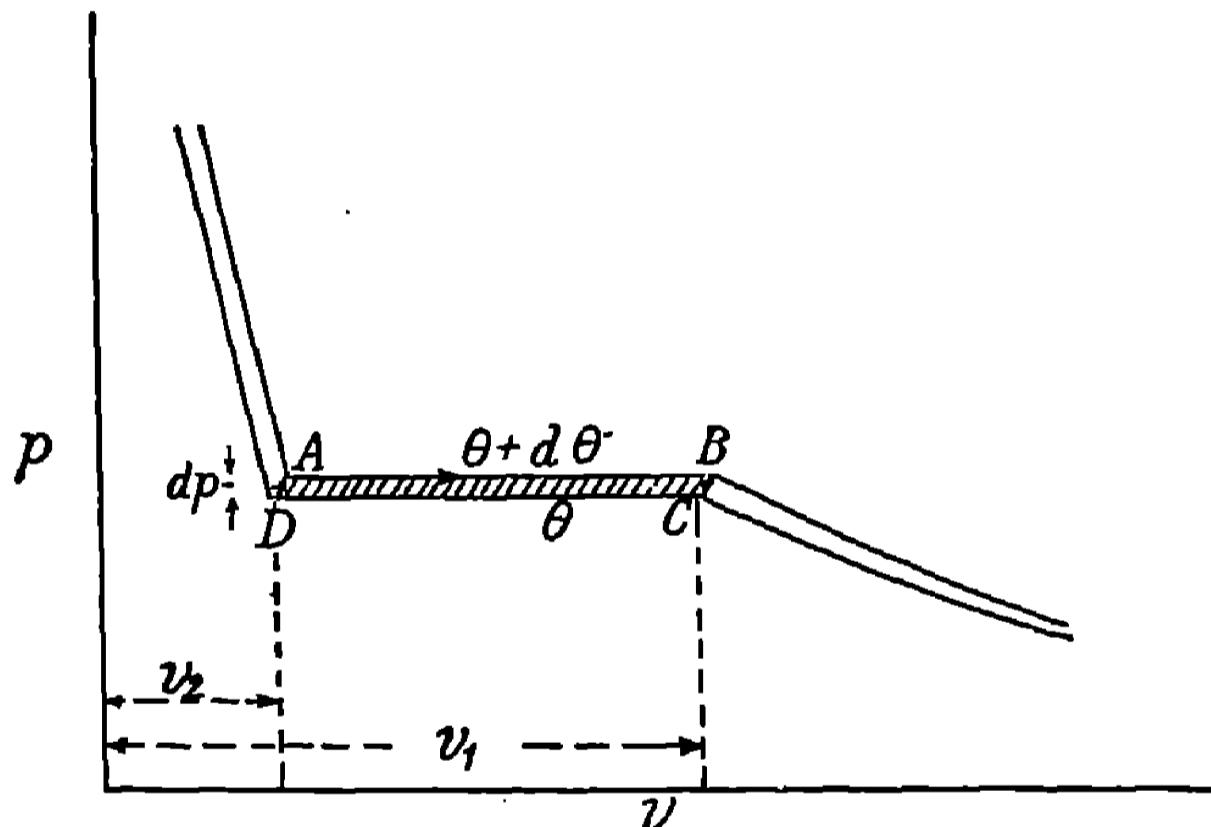
Fig. 8.—Effect of Pressure on Boiling-point

Next, by applying the Second Law of Thermodynamics to the cycle,

$$\left\{\frac{L}{\theta} + \frac{d}{d\theta}\left(\frac{L}{\theta}\right)\delta\theta\right\} - \left(\frac{L}{\theta}\right) + \frac{s_2 \cdot \delta\theta}{\theta} - \frac{s_1 \cdot \delta\theta}{\theta} = 0,$$

or $\qquad \dfrac{dL}{d\theta} - \dfrac{L}{\theta} + (s_2 - s_1) = 0.$ . . . . (13.21)

Hence, from (13.20) and (13.21), we have

$$\frac{L}{\theta} = (v_1 - v_2)\frac{dp}{d\theta},$$

or the elevation in boiling-point, $d\theta$, is given by

$$d\theta = \frac{\theta}{L}dp\,(v_1 - v_2). \qquad . . . . . (13.22)$$

Again, from (13.21), we have

$$s_1 = s_2 + \frac{dL}{d\theta} - \frac{L}{\theta}. \quad \ldots \ldots \quad (13.23)$$

As the critical temperature is approached, L decreases and its graph cuts the temperature axis at right angles; hence $\frac{dL}{d\theta} = \infty$, and so the specific heat of a saturated vapour approaches infinity as the critical temperature is approached.

13. Constants of the Thermo-electric Circuit.

The student should read the chapter on this subject in Part V before proceeding with this section. Consider two different metals A and B constituting a thermo-electric circuit with one junction at a temperature θ and the other at temperature $(\theta + \delta\theta)$. Then, if σ_A, σ_B are the Kelvin coefficients, and the Peltier coefficient at θ is P, applying the two laws of thermodynamics when a charge q is taken round the circuit, we have

$$\left(P + \frac{dP}{d\theta}\delta\theta\right)q - Pq + \sigma_A q\,\delta\theta - \sigma_B q\,\delta\theta = q\frac{dE}{d\theta}\delta\theta,$$

or

$$\frac{dP}{d\theta} + (\sigma_A - \sigma_B) = \frac{dE}{d\theta}, \quad \ldots \ldots \quad (13.24)$$

and

$$q\left\{\frac{P}{\theta} + \frac{d}{d\theta}\left(\frac{P}{\theta}\right)\right\} - \frac{qP}{\theta} + \frac{\sigma_A q\,\delta\theta}{\theta} - \frac{\sigma_B q\,\delta\theta}{\theta} = 0, \quad (13.25)$$

where $\frac{dE}{d\theta}\delta\theta$ is the thermo-electric Seebeck E.M.F. for a temperature difference $\delta\theta$ between the junctions. Eliminating σ_A and σ_B, we have

$$P = \theta\frac{dE}{d\theta},$$

and, eliminating P, we have

$$(\sigma_A - \sigma_B) = -\theta\frac{d^2E}{d\theta^2}.$$

These equations give a method of calculating the Peltier and Kelvin coefficients if $dE/d\theta$ and $d^2E/d\theta^2$ are known.

EXERCISES

1. Give an account of Carnot's cycle. Under what ideal conditions is a cycle strictly reversible?

2. Show that the efficiency of all strictly reversible cycles is the same. What important bearing has this fact on the generality of thermodynamical arguments?

3. State the Second Law of Thermodynamics. Upon what experimental facts is it based? Give one important example of its application.

4. Distinguish between the absolute scale of temperature and the gas scale. Show that for an ideal gas these are identical.

5. Deduce an expression for the change in freezing-point of a pure solvent with external pressure.

Find the change in the melting-point of ice when the external pressure is raised from one to two atmospheres, given that its latent heat of fusion is 80 cal./gm. and that the density of ice remains constant at 0·92 gm./c.c. [−0·007° C.]

6. Obtain an expression for the heat absorbed or evolved reversibly when a film subject to surface tension is taken round a reversible thermodynamical cycle.

Under what conditions are surface tension and surface energy per unit area equal?

7. Discuss the action of reversible primary cells from the thermodynamical standpoint. In what respects is a Daniell cell exceptional in its behaviour?

8. State briefly what you know concerning the nature of entropy, and deduce an expression for the difference in the specific heats of a liquid and its vapour at the boiling-point, in terms of its latent heat of vaporization.

CHAPTER XIV

Radiation

1. Introduction.

We have already stated in Chap. IV that if a hot body is placed in a vacuum so as to eliminate conduction and convection, it still loses heat. This is said to be due to **radiation**. It is supposed in elementary theory that the molecules, owing to their own heat vibration, send out waves which carry away energy; consequently the body eventually cools. Heat from the sun must reach the earth by radiation, since no material medium exists between the two bodies. Now during an eclipse of the sun, heat is cut off simultaneously with the light radiations. This indicates that light and heat radiations are similar and, in fact, heat radiation obeys the same general laws as light. If a spectrum is thrown on to a screen, with a powerful arc as a light source, and a thermometer with its bulb coated with lamp-black is moved across the spectrum, it will be found that little effect occurs when the thermometer is near the violet end of the spectrum. As, however, the red end is approached, the thermometer begins to rise, and this effect continues when the thermometer is placed beyond the red end and no *visible* radiations are falling upon it. It is then receiving heat radiation only, and is said to be in the **infra-red** portion of the spectrum (see Part III).

2. Simple Laws of Heat Radiation.

(i) *Angle of Incidence equals Angle of Reflection.*

To show that the angle of incidence equals the angle of reflection for heat rays, an apparatus is used as in fig. 1. A plane mirror M of speculum metal is equally inclined to the axes of two tubes. Opposite the end of one tube is placed a white-hot piece of platinum foil F, a thermopile T (see Part V) being used to receive the radiation reflected from the mirror. The galvanometer connected to the thermopile shows a large deflexion only when the mirror is turned so that the angle of incidence equals the angle of reflection.

(ii) *Inverse Square Law.*

To demonstrate that the intensity of the radiation falls off inversely as the square of the distance from the source, an apparatus is

used as in fig. 2. A cubical metal container, known as *Leslie's cube*, contains water, and is raised to a suitable temperature, the thermo-couple being presented to it at various distances as shown. The thermo-couple is fitted with a conical hood so that radiations are received from definite circular areas of the cube. It is then found that the deflexion
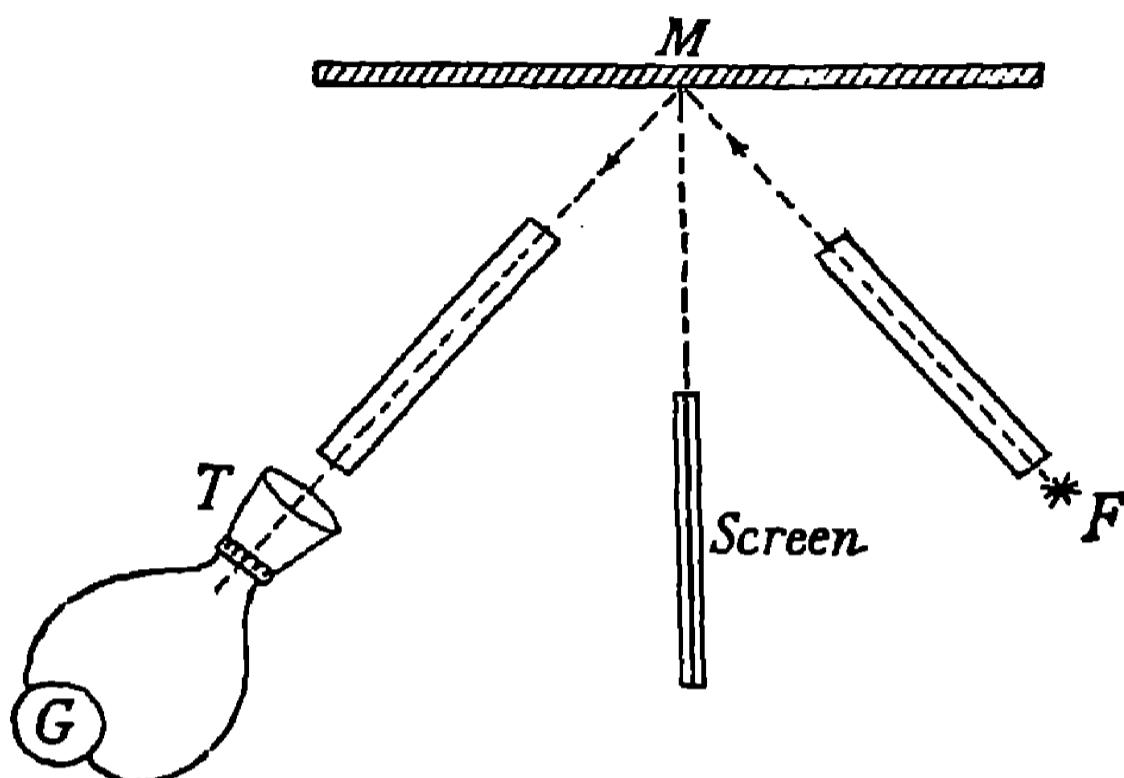
Fig. 1.—Law of Reflection for Heat Rays

of the galvanometer is independent of the distance of the thermo-couple from the cube over a moderate range. We proceed to show that this is consistent with an inverse square law.

If d is the perpendicular distance, the effect on the thermocouple will be of the form kA/d^n, where A is the effective area cut off by the hood, k is some constant of the apparatus, and n is the exponent we
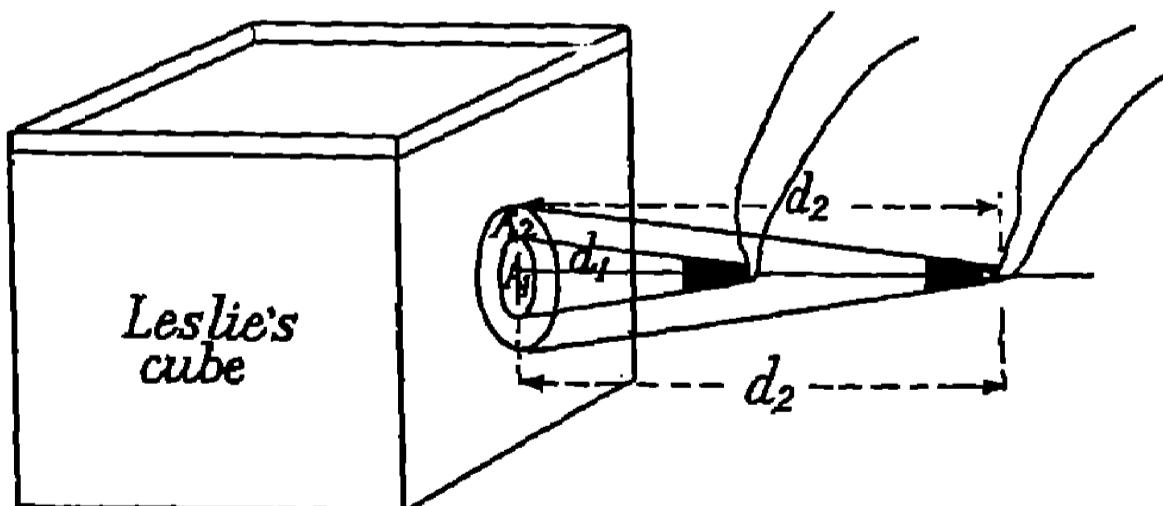
Fig. 2.—The Inverse Square Law

wish to find. For any two positions, the experiment shows that the effect is constant, so

$$kA_1/d_1{}^n = kA_2/d_2{}^n,$$

whence $$A_1/A_2 = (d_2/d_1)^n. \quad . \quad . \quad . \quad . \quad (14.1)$$

Now the two conical figures in fig. 2 are similar, and by the properties of similar cones

$$A_1/A_2 = (d_2/d_1)^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (14.2)$$

But (14.1) and (14.2) can only hold simultaneously if $n = 2$.

If the thermocouple is so far away from the cube that the side of the cube is smaller than the projection of the hood, the result no longer follows. Similarly, for very close distances the agreement is not good, since the intensity of emission decreases as the rays become highly inclined to the emitting surface.

(iii) *Focussing Properties*.

If two parabolic mirrors are set up as shown in fig. 3 on a common axis several metres apart and a hot platinum foil is placed at the focus
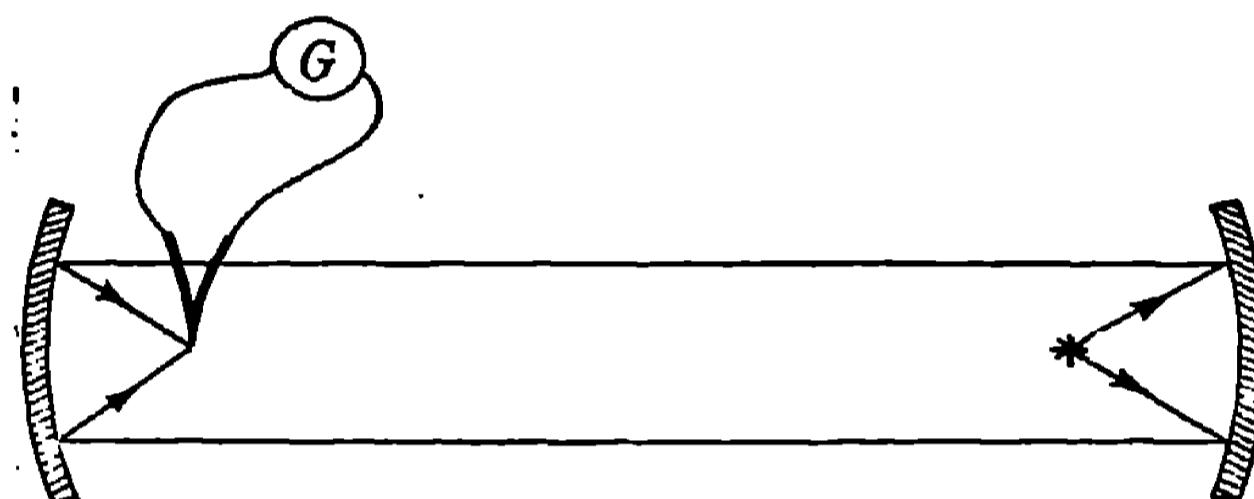
Fig. 3.—Focussing of Heat Radiation

of one mirror, an intense effect is produced in the thermocouple only when the latter is at the focus of the second mirror. It is striking to observe the deflexion of the galvanometer G decrease as the thermocouple is moved nearer the source but out of the focus.

3. Emission and Absorption of Radiation.

If the various sides of a Leslie's cube are coated with different materials such as lamp-black, highly polished metal, paper, and so on, it will be found on rotating the cube that although all the sides are at the same temperature some faces emit more radiant heat than others. Conversely, if a thermopile is covered with lamp-black, it is found to be far more sensitive to radiant heat than if its elements are highly polished. The general fact emerges that some substances emit and absorb radiant heat far more easily than others. Further, good radiators are good absorbers. A simple experiment to illustrate this is shown in fig. 4, which describes an apparatus due to Ritchie. A vertical U-tube containing coloured liquid is sealed at the ends to two equal cylinders A and B containing air. These cylinders have their faces coated with silver and lamp-black respectively, as shown. A third cylinder C is coated on one face with silver and on the other

with lamp-black, and C may be filled with hot water and inserted between A and B. Now, if the apparatus is arranged so that the silvered face of C radiates to the blackened face of B and consequently the blackened face of C radiates to the silvered face of A, it is found that no movement of the liquid occurs in the U-tube. This shows that although there is little heat radiated from C to B, what there is is all absorbed by B; conversely, although a large quantity of heat is radiated from C to A the latter, being silvered, absorbs very little. On rotating C so that silver radiates to silver and lamp-black to lamp-black, a large deflexion shows the superior radiating and absorbing properties of lamp-black.

A perfect absorber is one that absorbs all the radiant heat incident upon it and reflects none. Lamp-black constitutes the nearest approach to such a hypothetical substance, which is called a **perfectly black body.**
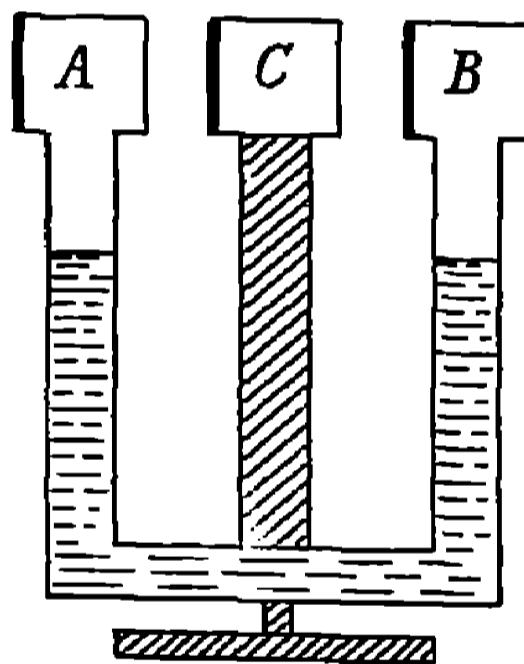
Fig. 4.—Absorption and
Radiation
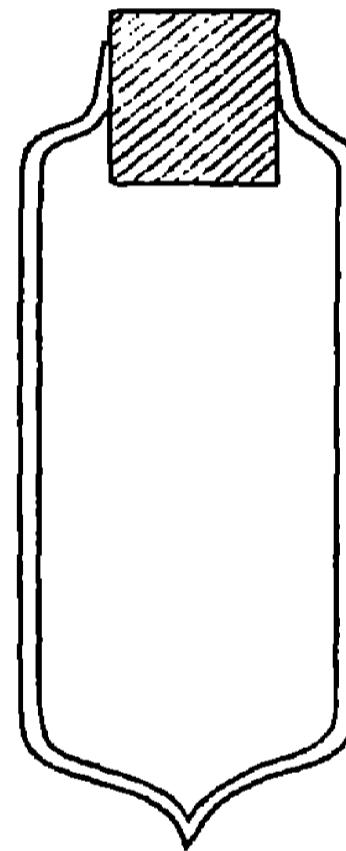
Fig. 5.—Dewar Vacuum
Flask

4. Applications of the Laws of Radiant Heat.

The student will be familiar with the use of brightly polished surfaces to minimize radiation and absorption. For example, teapots are usually highly polished. The most important example is perhaps the Dewar vacuum flask, in which heat losses by conduction, convection and radiation are reduced so much that liquid air, 200° C. below room temperature, may be kept in an ordinary room for over a day without completely evaporating. As shown in fig. 5, the Dewar flask consists of a double-walled glass vessel of cylindrical shape fitted with a long tapering cork. The inner sides of the glass walls are silvered, and the space between them finally evacuated. Heat conduction can occur then only along the top rim of the badly conducting glass or down the long tapering cork. Since air is prevented from reaching the inner

walls of the vessels, convection is almost non-existent. Radiation is reduced to a minimum by the silvering, which reflects the heat waves.

5. Stefan's Law of Radiation.

From experiments with different surfaces at different temperatures, Stefan was led to the conclusion that the quantity of heat radiated by a surface was proportional to the fourth power of the absolute temperature. This is **Stefan's Law of Radiation.** It is only strictly true for perfectly black bodies, the power varying for real bodies between 3 and 4 according to the nature of the surface. Boltzmann first placed the law on firm theoretical grounds. In mathematical terms, a body at absolute temperature T_2 is losing heat to its surroundings at temperature T_1 according to the relation

$$H = \sigma(T_2{}^4 - T_1{}^4), \quad \ldots \ldots \quad (14.3)$$

where σ is a constant termed *Stefan's constant*. The quantity $\sigma T_1{}^4$ is introduced since the body will be *receiving* heat from the surroundings equal in magnitude to this amount.

6. Planck's Radiation Law.

We have indicated that radiant heat is similar in behaviour to light. If radiant heat is passed through a prism, a spectrum is formed, just as for light. The prism must, however, be made of some material such as rock salt or fluor-spar, since glass absorbs the greater part of heat radiation. That substances may be transparent to visible light but opaque to heat radiation is shown by the glass fire-screen, by which the light rays are transmitted while the heat rays are absorbed. The converse is true in fogs, where infra-red radiation is transmitted under conditions where visible radiation is absorbed. This fact forms the basis of infra-red photography under misty conditions over large distances. Substances which absorb radiant heat are sometimes said to be **athermanous,** while those which transmit it are termed **diathermanous.**

Now it has long been known (see Part III, Chap. IX) that light consists of a wave motion and radiant heat is the same type of wave motion but of longer wave-lengths. It is of particular interest to examine how the heat energy contained in the radiant heat is distributed among the various wave-lengths present. The experiment was carried out by Lummer and Pringsheim, who detected the heat from the variation in electrical resistance of a platinum wire on which the heat was allowed to fall. The wire was included in one arm of a Wheatstone bridge; such a general arrangement is termed a **bolometer.** Radiant energy deviated by a fluor-spar prism was focussed by a mirror on the bolometer. The prism had previously been calibrated with a diffraction grating (see Part III, Chap. VII), so the wave-length of the

radiation was known for a given angle of deviation. The type of curves obtained is shown in fig. 6. A prominent feature of these curves is the hump indicating a maximum energy, which moves towards the region of shorter wave-lengths as the temperature of the black body radiator is increased. **Wien** showed that the radiation obeyed a **displacement law**,

$$\lambda_m \theta = \text{constant}, \quad \ldots \ldots \quad (14.4)$$

where λ_m is the wave-length of the maximum energy for a given absolute temperature θ. He also showed that the energy was distri-
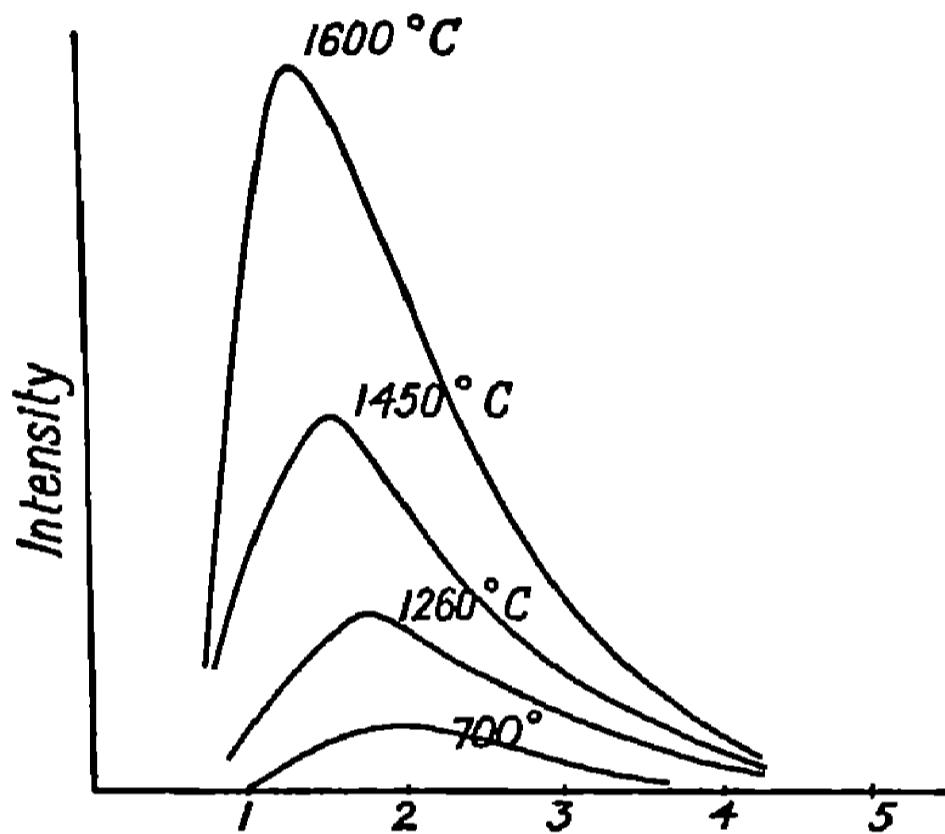
Fig. 6.—Spectrum of Radiant Heat

buted among the wave-lengths in accordance with the relation

$$E_\lambda d\lambda = c\lambda^{-5} f(\lambda\theta) d\lambda, \quad \ldots \ldots \quad (14.5)$$

where c is a constant. (In fig. 6, the abscissæ are wave-lengths, the unit being 1μ, or 10^{-4} cm.)

It was **Planck** who finally obtained the complete law, namely,

$$E_\lambda d\lambda = \frac{C_1 \lambda^{-5}}{e^{C_2/\lambda\theta} - 1} d\lambda, \quad \ldots \ldots \quad (14.C)$$

where C_1 and C_2 are constants.

The energy distribution observed experimentally by Lummer and Pringsheim was directly contradictory to what was expected theoretically from all previous physical principles, that is, from what is termed **classical theory**. Planck obtained his formula on the revolutionary theory that radiant heat is not emitted by the radiator nor absorbed by the absorber in continuous waves but in discrete packets of energy termed **quanta**. Thus, in 1900, the **quantum theory** and the era of Modern Physics were born.

7. Pyrometers for Measuring High Temperatures.

(i) *Féry Total Radiation Type.*

The pyrometers for measuring high temperatures depend on the heat absorbed, usually by a thermocouple, from a source radiating at high temperature, together with either Stefan's law or Planck's law. In the Féry total radiation type a concave polished copper mirror (fig. 7) focuses the radiations from an aperture in the side of the furnace, say, on to a thermocouple connected to a galvanometer. The thermocouple is usually calibrated by noting the deflexion of the galvanometer under the same conditions of standard distance when the temperature of the source is known by direct measurement. Of course, for very high temperatures this is not possible, and then Stefan's law must be extrapolated, that is, σ is given some average value for the source under consideration and Stefan's law is assumed to hold up to the highest temperatures to be determined. In this way, the **solar constant,** that is, the heat radiated per unit area per second by the sun's surface, indicates that if the conditions are those of Stefan's law, the mean temperature of the sun's surface is about 6000° C.
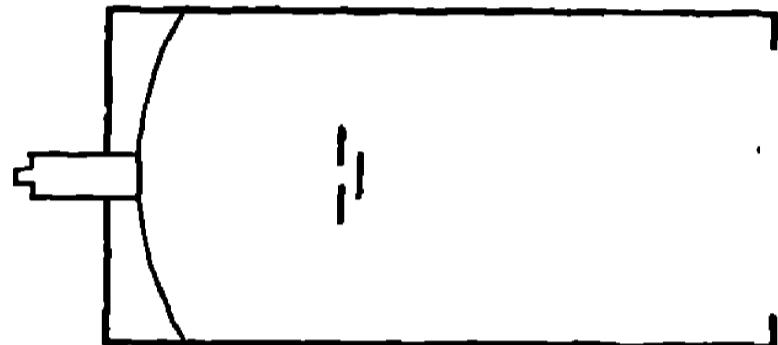
Fig. 7.—Féry Total Radiation Pyrometer

We may note that a small hole in the side of a furnace emits radiations which are likely to be very similar to those emitted by a perfectly black body at the same temperature. This is generally known as the *Law of Cavity Radiation.* We illustrate its validity as follows. Consider a ray passing *into* a small hole in a furnace. After incidence on the inner wall of the furnace, a certain portion of the radiant energy will be absorbed and a certain portion will be reflected. A perfectly black body would have absorbed all the radiation; the enclosure eventually approximates to this, for the reflected ray will strike the inner wall of the enclosure and again be partially absorbed. The chance of any appreciable portion of the radiant energy emerging again from the enclosure is extremely small, so the interior behaves as a perfectly black body. Conversely, the totality of rays which are emitted from the inner wall of the furnace and escape from the small aperture will be similar to those emitted by a perfectly black body.

(ii) *Disappearing Filament Pyrometer.*

This type depends on the use of Planck's law. A certain region of the spectrum is isolated by simply interposing a sheet of red glass which limits the spectrum to a small range of wave-lengths. Then for the eye to estimate as equal the brightness of two sources compared simultaneously, the energy in the same range of wave-lengths, and con-

sequently, by Planck's formula, the temperatures, must be the same.

In the disappearing filament pyrometer, a diagram of which is given in fig. 8, the filament of an electric lamp is seen against the background of the image of the opening in the furnace.   If the temperature of the filament is less than that of the furnace, the filament
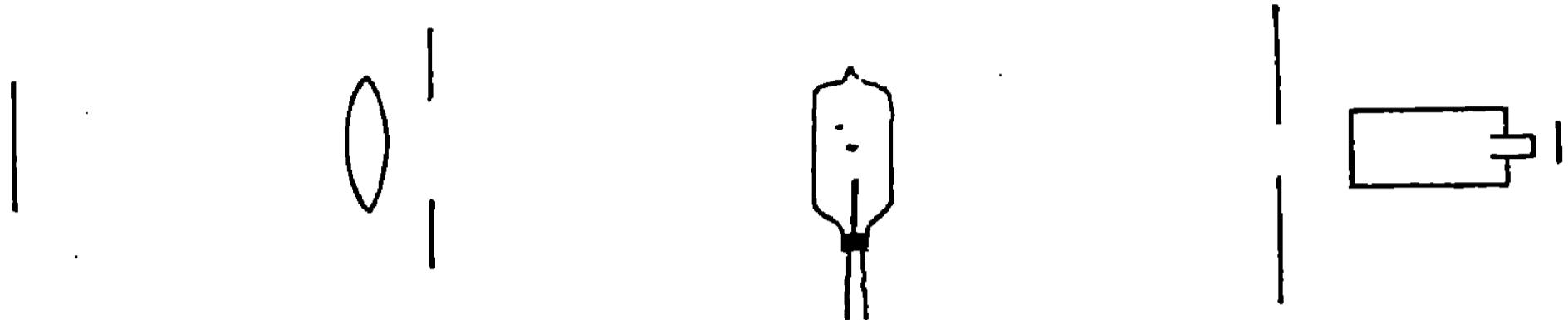
Fig. 8.—Disappearing Filament Pyrometer

appears darker than the background. By using a variable resistance, the current through the filament is adjusted until it becomes invisible or disappears against the background. The ammeter has been calibrated already against surfaces of known temperature, so that the temperature is read off directly.

EXERCISES

1. Write a short essay on Radiant Heat.

2. By what experiment may it be shown that the intensity of heat radiated from a source falls off inversely as the square of the distance from the source ?

What laws govern the emission and absorption of heat radiation and on what experiments are they based?

3. Describe the Dewar vacuum flask, explaining carefully how heat losses are reduced to a minimum.

4. State Stefan's Law of Radiation and describe some form of total radiation pyrometer.

5. Give an account of the distribution of energy in the spectrum of black-body radiation. What is the particular importance of this investigation?

6. Describe the disappearing filament pyrometer, explaining carefully the physical principles upon which it is based.

7. What is meant by *Wien's displacement law* ?

How would you determine the solar constant ?

EXAMPLES

REQUIRED CONSTANTS

The numbers in brackets at the end of each question indicate which constants are to be used from the Table given below

1. Coefficient of linear expansion of wrought iron, 1.19×10^{-5} per °C.
2. Coefficient of linear expansion of brass, 1.89×10^{-5} per °C.
3. Coefficient of linear expansion of copper, 1.67×10^{-5} per °C.
4. Coefficient of linear expansion of aluminium, 2.55×10^{-5} per °C.
5. Coefficient of linear expansion of steel, 2.00×10^{-5} per °C.
6. Coefficient of linear expansion of glass, 9.00×10^{-6} per °C.
7. Coefficient of cubical expansion of mercury, 1.82×10^{-4} per °C.
8. Coefficient of cubical expansion of ether, 1.63×10^{-3} per °C.
9. Young's Modulus for brass, 10^{12} dynes/sq. cm.
10. Young's Modulus for steel, 2×10^{12} dynes/sq. cm.
11. Density of glycerine at 15° C., 1.26 gm./c.c.
12. Density of mercury at 15° C., 13.56 gm./c.c.
13. Density of steel at 15° C., 8.00 gm./c.c.
14. Specific heat of lead, 0.03.
15. Specific heat of rubber, 0.50.
16. Latent heat of fusion of ice, 80 cal./gm.
17. Latent heat of condensation of steam, 540 cal./gm.
18. Melting-point of rubber, 310° C.
19. Melting-point of lead, 335° C.
20. Joule's mechanical equivalent of heat, 4.18×10^7 ergs/cal.

1. A Fahrenheit thermometer and an accurate Centigrade thermometer register 161° and 70·5° respectively when placed in the same enclosure, which is at uniform temperature. What is the error in the Fahrenheit thermometer?

2. A simple compensated pendulum consists of two wrought-iron rods and a brass rod with horizontal connecting pieces. Draw a diagram of the vertical arrangement of the rods and calculate the total length of the iron rods, given that the brass rod is 3 ft. long at 15° C. (1, 2.)

3. Find the fall in temperature required to cause a clock to gain 1 sec. per hour if the pendulum is made of wrought iron. (1.)

4. If a shrinkage fit is just obtained when a copper ring and an aluminium disk are both immersed in " dry ice " (solid carbon dioxide), find the temperature of the latter, assuming that the contraction is uniform and that the ratio of the radius of the disk to the internal radius of the ring at 20° C. is $(1 \cdot 00510/1 \cdot 00334)^{\frac{1}{2}}$. (3, 4.)

5. A thick vertical glass rod is held rigidly at its base. A horizontal brass rod of cross-section 1 sq. cm. has one end fixed rigidly in a wall, while its free end is clamped to the end of the glass rod. If the glass rod fractures under a horizontal pull of more than 100 lb., determine whether it will fracture if the brass rod is suddenly cooled through 10° C. (2, 9.)

6. Prove that the coefficients of surface and volume expansion of a solid are equal approximately to twice and three times the coefficient of linear expansion.

7. A steel rod of length 50 cm. and area of cross-section 1 sq. cm. has concentrated masses each of 2000 gm. attached to its ends. Neglecting the weight of the rod, find the speed at which the rod must be rotated about a vertical axis passing through its middle point so that the tension in the rod shall equal that produced by clamping the two masses rigidly and then cooling the rod through 100° C. (5, 10.)

8. In Ques. 7, find the error, in the tension at the middle point, introduced by neglecting the weight of the rod. (13.)

9. Two rods of length l_2 and coefficient of linear expansion a_2 are connected freely to a third rod of length l_1 and coefficient of linear expansion a_1 to form an isosceles triangle, and the arrangement is suspended on a knife-edge at the mid-point of l_1 which is horizontal. What relation must exist between l_1 and l_2 if the apex of the isosceles triangle is to remain at a constant distance below the point of suspension as the temperature changes?

10. A copper cylinder has a small hole in the side at a height of 10 cm. from the base. It is filled with ether to within 1 mm. of the hole. What must be the rise in temperature for the ether to commence to escape from the hole? (3, 8.)

11. A glass weight thermometer contains 79·4 c.c. of glycerine at 15° C. If 4·10 gm. of glycerine escape when the thermometer is raised to 100° C., find the absolute coefficient of cubical expansion of glycerine. (6, 11.)

12. A barometer stands at a height of 76·00 cm. when the room temperature is 15° C. Find the height registered when the tempera-

ture sinks to 5° C., the external barometric pressure remaining unaltered.   (7.)

13. A narrow L-shaped silica tube is of uniform cross-section and is closed at the ends, the longer limb being twice the length of the shorter. It is freely suspended at the bend, and the shorter limb is just filled with a liquid the coefficient of cubical expansion of which is $3 \cdot 10^{-3}$ per °C. rise of temperature. If the mass of the liquid is nine times that of the shorter limb and the apparatus is cooled through 100° C., show that the relation between the angles at which the shorter limb is inclined to the vertical at the two temperatures is given by $\tan \alpha_1 : \tan \alpha_2 :: 157 : 130$.

14. A silica sinker which weighs 100 gm. in air is suspended from a balance arm and immersed in water at 4° C., whereupon a loss in weight of 37·59 gm. is observed. On raising the water to 80° C. the loss in weight changes to 36·49 gm. Find the density of the water at 80° C. and the mean coefficient of cubical expansion of water between 4° and 80° C.

15. A piece of iron and a piece of copper each of weight 50 gm. are soldered together and placed in a hypsometer at 100° C. They are then removed and dropped quickly into a copper calorimeter of weight 50 gm. containing 50 gm. of water at 15° C., whereupon the temperature rises to 28·35° C. On repeating the experiment, but with 100 gm. of water in the calorimeter, the temperature rises to 22·55° C. Find the specific heat of iron and of copper.

16. A small cylindrical copper calorimeter of weight 10 gm. and specific heat 0·094 contains 10 gm. of water at 35° C., the temperature being registered by a thermometer inserted in the calorimeter. This thermometer is removed as a second thermometer which is registering a room temperature of 15° C. is inserted. The final temperature registered by the second thermometer is 33·35° C. The first thermometer is then replaced and shows a temperature of 32·00° C., while the second thermometer shows a temperature of 32·05° C. Find the water equivalent of the second thermometer.

17. A given volume of fresh water is placed in a calorimeter A, and an equal volume of sea-water is placed in an identically similar calorimeter B. Taking the density of the fresh water as unity and that of the sea water as 1·05 gm. c.c., find the specific heat of the latter if the times taken for the two liquids to cool through 20° C. are 1800 sec. and 1776 sec. respectively.

18. In a Joly differential steam calorimeter, the volume of each sphere is 500 c.c. and the excess weight of water condensed on the sphere containing the gas is 0·1 gm. Find the specific heat of the gas at constant volume if its initial temperature was 15° C. and its density is $6·00 \cdot 10^{-3}$ gm. c.c.   (17.)

(F 821)   **10**

19. From the following data obtained by using Regnault's apparatus for the specific heat of a gas at constant pressure, find the specific heat of dry air at constant pressure: mass of air passed 32·00 gm., temperature of oil bath 150·00° C., initial temperature of calorimeter 15·00° C., final temperature of calorimeter 25·40° C., water equivalent of calorimeter and contents 100·00 gm.

20. A metal cube of side 10 cm. is maintained at a uniform temperature. It is supported from below by an exactly similar cube of wood and suspended from above by a metal wire 10 cm. long and of cross-section 1 sq. mm. Compare the amounts of heat conducted through wood and wire respectively if their thermal conductivities are 5×10^{-4} and 9×10^{-1} C.G.S. units respectively.

21. A square glass window of side 6 m. and thickness 1 cm. is supported at the inner edge of a metal frame 6 cm. wide and 6 cm. thick. If the thermal conductivities of glass and metal are $2·5 \times 10^{-3}$ and $2·6 \times 10^{-1}$ C.G.S. units respectively, compare the contributions to the heat lost through the window and the frame.

22. A slab consists of two parallel layers of different materials 4·0 and 2·0 cm. thick and of thermal conductivities 0·54 and 0·36 C.G.S. units respectively. If the opposite faces of the slab are at 100° C. and 0° C., calculate the temperature at the surface dividing the two materials.

23. A pool of molten sulphur has a crust 10 cm. thick and is cooling by exposure to the air, which is at a mean temperature of 4° C. Given that the melting-point of sulphur is 444° C., that its latent heat of fusion is 9 cal./gm., and that its density is 2·00 gm./c.c., find its thermal conductivity if it takes 4 hours for the crust to increase to 20 cm. thick.

24. In a certain Bunsen's ice calorimeter the inner tube is a right circular cylinder with a flat end, the length being 6·0 cm. and the internal and external diameters 2·40 and 2·80 cm. respectively. When a current of air at 4° C. is passed steadily through the tube, the mercury is found to creep along the capillary tube of diameter 2 mm. at the rate of 2·70 cm. per min. Given that the density of the ice is 0·92 gm./c.c., find the thermal conductivity of the material of the inner tube. (16.)

25. In determining the thermal conductivity of a plate (area 75 sq. cm., thickness 2 mm.) of a poor conductor by Lees' method, the steady temperatures of the two sides of the conductor were 96° C. and 46° C. Find the thermal conductivity of the poor conductor, given that the mass of the metal disk radiating at 46° C. was 1000 gm., its specific heat 0·094, and its rate of cooling at 46° C. was 7·20° C./min.

26. A rubber tube of internal and external radii 0·90 and 1·10 cm. and of length 50 cm. is immersed in a calorimeter whose total water equivalent, including that of its contents, is 100 gm. If the temperature of the calorimeter rises from 15° C. to 35° C. in 38 sec. when a current of steam at 100° C. is blown through the rubber tube, find the thermal conductivity of the rubber.

27. Steam at 100° C. is blown into a cavity in a block of metal of an alloy that melts at 90° C. Given that the latent heat of fusion of the alloy is 5 cal./gm., compare the rates of increase of the relative amounts of molten metal and condensed water when melting is proceeding uniformly. (17.)

28. The brakes are suddenly applied to a train of mass 150 tons and the speed is thereby reduced from 60 to 40 m.p.h. Determine the amount of heat produced in calories. (20.)

29. Two equal lead bullets collide head-on. Show that if they stop and just reach their melting-point under the heat generated at the impact, their relative velocity must have been nearly 1800 ft./sec. The temperature of the bullets just before impact was 35° C. (14, 19, 20.)

30. The brakes are suddenly applied to a lorry of mass 2 tons and the vehicle skids. Determine the least speed at which the lorry was travelling if the rubber in contact with the road just begins to melt at the instant the lorry is reduced to rest. Effective mass of rubber in contact with road is 4 lb., and initial temperature of tyres is 10° C. (15, 18, 20.)

31. What is the least height from which a piece of lead must be dropped so that it shall just start to melt under the heat generated at the impact? Initial temperature of lead just before impact is 35° C. (14, 19, 20.)

32. Two cubes of ice, each of mass 50 lb., have two of their faces rubbed together by a machine working at 0·5 h.p. Determine how long it will take for the blocks to melt to half their size under the friction produced. (16, 20.)

33. Using Callendar's continuous flow method, it is found that in one experiment the thermometers register 15·00° C. and 25·00° C. respectively when the rate of flow of water is 36,000 gm./hour. To maintain, however, the second thermometer at 42·5° C. when water is supplied at a temperature of 32·5° C. (and electrical power is supplied at the same rate), the flow must be increased by 72 gm./hour. Compare the specific heat of water at 20° C. and 37·5° C.

34. A copper calorimeter of mass 200 gm. and specific heat 0·094 contains 100 gm. of a liquid immersed in which is a coil of wire carrying a current of 4 amp. under a potential difference of 4 volts. If

the temperature rises 10° C. in 140 sec., find the specific heat of the liquid, neglecting heat losses and the heat capacity of the wire. (20.)

35. In Ques. 34, the temperature is allowed to rise until the liquid boils, and it is then found that after 250 sec. the weight of the liquid has been reduced to 90 gm. Find the latent heat of vaporization of the liquid.

36. A narrow glass tube containing a column of mercury is sealed at both ends while the tube is horizontal and a volume of air is enclosed at each end, the volume at one end being twice that at the other. The barometric pressure is 76 cm. of mercury. On arranging the tube vertically the volumes of air at the two ends change to the ratio of three to one. Find the length of the enclosed mercury column.

37. In the process of the evacuation of a vessel by an ordinary air pump the pressure drops from an initial value of 76 cm. of mercury to 60 cm. after 10 strokes. How many strokes will be required to reduce the pressure to 10 cm.?

38. Into a vessel of volume V maintained at a temperature T three gases are passed. If the three gases had initial pressures, volumes and temperatures (p_1, V_1, T_1), (p_2, V_2, T_2), and (p_3, V_3, T_3) respectively, find the final pressure.

39. A flask containing 1000 c.c. of liquid air is placed under a closed vessel containing 1000 c.c. of gaseous air at a pressure of 1 atmosphere. If 1 c.c. of liquid air gives on evaporation 1000 c.c. of gaseous air at a pressure of 1 atmosphere at a temperature of —200° C., find at approximately what temperature the closed vessel will burst when all the liquid air has evaporated. The bursting pressure of the vessel is 3000 atmospheres.

40. Given that an explosion will occur in a room of volume 2000 c. ft. if a hydrogen content greater than 1 per cent by volume is present, determine whether it would be safe to light a pipe in the room if a leaky hydrogen cylinder of capacity 1 c. ft. standing in a box of ice and initially at a pressure of 100 atmospheres is observed to read 75 atmospheres. The room temperature is 15° C. and the barometric pressure 1 atmosphere.

41. Find the value of Joule's mechanical equivalent of heat from the following data: density of hydrogen at N.T.P. is $9 \cdot 00 \times 10^{-5}$ gm./c.c., its specific heat at constant volume is 2·40, and C_p/C_v is 1·40.

42. The space above the mercury in a barometer tube contains some air and saturated vapour, the pressure of the latter being 3·0 cm. of mercury. If the barometric pressure is 76 cm. of mercury and the barometer tube is reading 70 cm. of mercury, what will it read

when by depression of the tube the space above the mercury has been reduced to one-quarter of its original volume?

43. After collecting 500 c.c. of gas over water in a burette with a tap at the top, the tap is opened to an evacuated vessel and the total volume of the expanded gas becomes 1000 c.c. If the temperature is kept constant and the vapour remains saturated, find the final total pressure, given that the initial total pressure was 762 mm. of mercury and that the saturation vapour pressure of water at the temperature of the experiment was 17 mm. of mercury.

44. Using a Victor Meyer's vapour density apparatus, the weight of liquid used was 0·250 gm. and the displaced air, which was collected over water at 15° C., occupied a volume of 250 c.c. If the barometric pressure was 76 cm. of mercury and the saturated vapour pressure of water at 15° C. is 1·28 cm. of mercury, find the vapour density of the liquid at 0° C. and a pressure of 76 cm. of mercury.

45. A gram-molecule of helium at 20° C. is suddenly subjected to a pressure ten times its initial value. Find the final temperature momentarily attained. C_p/C_v for helium is 1·67.

46. Referring to Ques. 45, find the work done during the compression, given that the gas constant R for a gram-molecule is 2·0 cal.

47. Find the final temperature reached and the work done if a gram-molecule of a gas expands at constant pressure until its volume is doubled. Initial temperature of gas is 87° C.

48. In Ques. 47, find the work done if the expansion is isothermal.

49. Find the root mean square velocity of a hydrogen molecule at N.T.P., given that the density of hydrogen under these conditions is $9·00 \times 10^{-5}$ gm./c.c. (12.)

50. An observation of Tyndall showed that the heat radiated from a piece of platinum foil at 1200° C. was 11·7 times the amount radiated by the foil at 525° C. Is the observation in agreement with Stefan's law of radiation?

ANSWERS AND HINTS FOR SOLUTION

1. $C/100 = (F - 32)/180$; $2 \cdot 1°$ F.

2. If combined length of iron rods is $(l_1 + l_2)$, then $(l_1 + l_2)a_1 = 3a_2$ for compensation; $4 \cdot 8$ ft.

3. $t_1 = 2\pi(l/g)^{\frac{1}{2}}$, $3599t_1/3600 = 2\pi\{l(1 - a\theta)/g\}^{\frac{1}{2}}$; $47°$ C.

4. If r_0 is common radius at lower temperature, considering the surface expansion, $\pi r_1^2 = \pi r_0^2(1 + 2a_1\theta)$, $\pi r_2^2 = \pi r_0^2(1 + 2a_2\theta)$; $-80°$ C.

5. Pull in dynes is $P = EAa\theta$, where E is Young's Modulus in dynes/sq. cm. and A is area of cross-section. Yes, 424 lb.

6. $S = S_0(1 + \beta\theta)$, also $S = l_\theta^2 = l_0^2(1 + a\theta)^2$; expanding and neglecting a^2, $\beta = 2a$. Similarly, $\gamma = 3a$.

7. Tension in rod on cooling is $P = EAa\theta$; tension due to centrifugal force would be $Mr\omega^2$, where ω is the angular velocity of rotation. Hence $\omega = (EAa\theta/Mr)^{\frac{1}{2}} = 283$ rad./sec.

8. Let m be mass of rod per unit length; element dx distant x from axis of rotation contributes centrifugal force $m \cdot dx \cdot x \cdot \omega^2$. Total centrifugal force contributed by whole rod is therefore $m\omega^2 \int_0^r x\,dx = \frac{1}{4}M_r \cdot r\omega^2$, where M_r is mass of whole rod. Hence effect in Ques. 7 is to increase M by $M_r/4$.

9. Distance d of apex below knife-edge is given by $d^2 = l_2^2 - l_1^2/4$ or $4d^2 = 4l_2^2 - l_1^2$. Differentiating to find change in d for change in l_1 and l_2, $8d \cdot dd = 8l_2 \cdot dl_2 - 2l_1 \cdot dl_1$. Hence for $dd = 0$, $4l_2 \cdot dl_2 = l_1 \cdot dl_1$, that is, $4l_2 \cdot l_2 a_2 = l_1 \cdot l_1 a_1$; $l_1^2 : l_2^2 :: 4a_2 : a_1$.

10. Let height of ether from base at instant of escape be h; then for cylinder $\pi r^2 h = \pi r_0^2 \cdot 10(1 + \gamma_1\theta)$; similarly for ether $\pi r^2 h = \pi r_0^2(9 \cdot 9)(1 + \gamma_2\theta)$; $6 \cdot 4°$ C.

11. $\gamma_l = (m_0 - m_t)/(m_t \cdot t) + \gamma_g \cdot m_0/m_t$; $5 \cdot 31 \times 10^{-4}$ per °C.

12. Since external pressure remains constant $\rho g h = \rho' g h'$, also $\rho = \rho'(1 + \gamma t)$; $75 \cdot 86$ cm.

13. Let length of short arm be $2l$; for equilibrium take moments about the bend. If w is the weight of shorter limb:
    Case 1. $(w + 9w) \cdot l \sin a_1 = 2w \cdot 2l \cos a_1$.
    Case 2. $w \cdot l \sin a_2 + 9w(2l - l_0) \sin a_2 = 2w \cdot 2l \cos a_2$, where l_0 is given by $l_t = 2l = 2l_0(1 + 3 \times 10^{-3} \times 100)$, or $l_0 = 10l/13$. Hence $\tan a_1 : \tan a_2 :: 157 : 130$.

14. $0 \cdot 971$ gm./c.c.; $3 \cdot 93 \times 10^{-4}$ per °C.

15. $(50s_1 + 50s_2)71 \cdot 65 = (50s_2 + 50)13 \cdot 35$; $(50s_1 + 50s_2)77 \cdot 45 = (50s_2 + 100)7 \cdot 55$; $0 \cdot 11$, $0 \cdot 095$.

16. Let W be water equivalent of second thermometer; when first thermometer reads 35·00° C., second thermometer would have read 35·05° C. Taking temperature differences on scale of second thermometer and equating heat gained by thermometer to heat lost by calorimeter and water:

$$W(33·35 - 15) = (10 \times 0·094 + 10)(35·05 - 33·35); \quad 1·01 \text{ gm.}$$

17. $M_1s_1/M_2s_2 = t_1/t_2$; 0·94.

18. $Wc_v\theta = wL$; 0·21.

19. $Wc_p\{150 - (25·4 + 15)/2\} = 100(25·4 - 15)$; 0·25.

20. Apply relation $Q = -kA\,d\theta/dx$ to wood and wire respectively, where Q is quantity of heat conducted per sec. through area A by substance of thermal conductivity k, and temperature gradient $d\theta/dx$ is assumed linear; 50 : 9.

21. As in Ques. 20; 1·43 : 1.

22. Let θ be temperature of interface; then if Q is quantity of heat flowing through unit area of slab per sec. for first layer, $Q = 0·54(100 - \theta)/4 = 0·36(\theta - 0)/2$ for second layer; 43° C. approx.

23. $Qt = -kA\,d\theta/dx \cdot t = mL = Ad\rho L$; $4·26 \times 10^{-4}$ cal. cm.$^{-1}$ sec.$^{-1}$ °C.$^{-1}$.

24. Volume creep in capillary is $\pi \times 10^{-2} \times 2·70/60$ c.c./sec. If mass of ice melted per sec. is m, change in volume produced is $m(1/0·92 - 1)$. Hence heat received per sec. $Q = mL = 0·92 \times 80 \times \pi \times 10^{-2} \times 2·70/0·08 \times 60$. But $Q = -kA\,d\theta/dx = 4k(2\pi \times 1·3 \times 6 + \pi \times 1·3 \times 1·3)/0·2$; $1·2 \times 10^{-1}$ cal. cm.$^{-1}$ sec.$^{-1}$ °C.$^{-1}$.

25. $Q = -kA\,d\theta/dx = ms\,d\theta/dt$; $6·0 \times 10^{-4}$ cal. cm.$^{-1}$ sec.$^{-1}$ °C.$^{-1}$.

26. $k = (Q/t)/\{2\pi rl(T_1 - T)/(r_2 - r_1)\}$; $4·5 \times 10^{-4}$ C.G.S. units.

27. $m_1L_1 + m_1 \cdot 10 = m_2L_2$; 110 : 1.

28. $\frac{1}{2}m(v_2{}^2 - v_1{}^2) = JH$; $7·3 \times 10^6$ cals.

29. Let vel. of each bullet be v. Then $2 \cdot \frac{1}{2}mv^2 = JH = J \cdot 2ms\theta$.

30. $\frac{1}{2}mv^2 = ws\theta J$; 74·6 m.p.h.

31. $mgh = ms\theta J$; 3·83 kilometres.

32. Rate of working = 0·5 h.p. = 373 watts = $3·73 \times 10^9$ ergs/sec. Heat required is $50 \times 1000 \times 80/2·2$; 5·7 hours nearly.

33. $I^2R = m_1s_110 = m_2s_210$; 0·998.

34. 0·35.

35. 96 cal./gm.

36. Let x be length of mercury column; then if whole length of tube is $x + 3l$, applying Boyle's law, if p_1 and p_2 are pressures in volumes above and below mercury respectively, $p_1 \times 9l/4 = 76 \times 2l$; $p_2 \times 3l/4 = 76 \times l$; $x = p_2 - p_1 = 33\frac{7}{9}$ cm.

37. If volume of vessel is V and volume of cylinder of pump is v, pressure at end of first stroke is given by $p_1(V + v) = pV$, while at end of second stroke $p_2(V + v) = p_1V = pV^2/(V + v)$, or pressure at end of nth stroke is $p_n = p\{V/(V + v)\}^n$; 86 strokes.

38. $T(p_1 V_1/T_1 + p_2 V_2/T_2 + p_3 V_3/T_3)/V$.

39. $-54°$ C. approx.

40. $1\cdot 3$ per cent; no.

41. Use $c_p - c_v = R/J$ and $pV = RT$; $4\cdot 3 \times 10^7$ ergs/cal.

42. Apply Boyle's law; 61 cm.

43. $389\cdot 5$ mm. of mercury.

44. $1\cdot 07 \times 10^{-3}$ gm./c.c.

45. $p^{(1-\gamma)/\gamma}.\, T = $ constant; $465°$ C.

46. Work done is $W = (p_2 V_2 - p_1 V_1)/(\gamma - 1) = R(T_2 - T_1)/(\gamma - 1)$; 1328 cal.

47. $447°$ C.; 720 cal.

48. Work done is $W = RT \log_e v_2/v_1$; 499 cal.

49. $V = (3p/\rho)^{\frac{1}{2}}$; $1\cdot 84 \times 10^5$ cm./sec.

50. Yes; $(1200 + 273)^4/(525 + 273)^4$ is $11\cdot 7$ approx.

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